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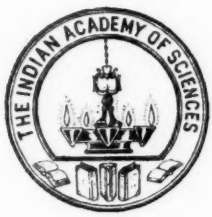

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ON $v(k)$

By S. S. Pillai

Received March 8, 1939
(Communicated by Dr. S. Chowla)

Let $v(k)$ denote the least value of s for which every n is representable in the form

$$n = \pm x_1^k \pm x_2^k \pm \cdots \pm x_s^k, \tag{1}$$

and V (k) denote the least value of s for which every sufficiently large n is representable in the above form.

Further let $\Gamma_1(k)$ be the function in this problem corresponding to Hardy-Littlewood's $\Gamma(k)$ in Waring's Problem.

The object of this note is to prove the following :—

Theorem I. V $(k) \geqslant [\Gamma(k)/2]$, when $k = 2^\theta$, $3 \cdot 2^\theta$, or $p^\theta(p-1)$.

Theorem II. V $(k) \geqslant \Gamma(k)$, when k is odd or $k = \frac{1}{2} p^\theta (p-1)$.

Theorem III. If $k = 2^\theta \cdot m$, where $(m, 2) = 1$,

then V $(k) \geqslant$ Max. $\{2^{\theta+1}, \Gamma(m)\}$.

Theorem IV. $v(k) \leqslant$ V $(k) + 1$.

Theorem V. V $(2) = 3$.

Perhaps $v(k) =$ V (k) ; and V $(k) \geqslant [\Gamma(k)/2]$ in all cases.

If the smallest prime of the form $kn + 1$ is $0(k^{1+\epsilon})$ for every $\epsilon > 0$, which is very plausible, it easily follows that $\underline{lim}\ \Gamma(k) = \infty$, and hence from Theorem III, we get that

$$\underline{lim}\ \text{V}(k) = \infty$$

(1) If P stands $p^{\theta+1}$ or $2^{\theta+2}$ according as $k = p^\theta(p-1)$ or $k = 2^\theta$ or $3 \cdot 2^\theta$, then when $(x, \text{P}) = 1$,

$$x^k \equiv 1 \pmod{\text{P}}.$$

So if $n \equiv \pm x_1^k \pm \cdots \pm x_s^k \pmod{\text{P}}$
is solvable for every n, then $s = [\text{P}/2]$
So $\Gamma_1(k) \geqslant [\text{P}/2]$. But $\Gamma(k) = \text{P}$.

From this Theorem I follows.

(2) Let $k = \frac{1}{2} p^\theta (p-1)$

Then if $(x, p) = 1$, $x^k \equiv \pm 1 \pmod{p^{\theta+1}}$.

So, as before $\Gamma_1(k) \geqslant \frac{1}{2}(p^{\theta+1} - 1)$.

Hence V $(k) \geqslant \Gamma(k)$; for in this case $\Gamma(k) = \frac{1}{2}(p^{\theta+1} - 1)$.

(3) Let k be odd.

Then, if $x^k \equiv a \pmod{M}$ is solvable,

$$x^k \equiv -a \pmod{M} \text{ is also solvable.}$$

So $\Gamma_1(k) = \Gamma(k)$ in this case.

Hence $V(k) \geqslant \Gamma(k)$.

From (2), (3), Theorem II follows.

If $k = m\,l$, then $\Gamma_1(k) \geqslant \text{Max.}\{\Gamma_1(m), \Gamma_1(l)\}$.

From this and Theorems I and II, Theorem III follows.

Let $N(k)$ be the integer from which every integer is representable in the form (1) when $s = V(k)$.

If $a < N(k)$, we can find y so that $a + y^k > N(k)$.

From this Theorem IV follows :*

$2 \cdot 3^{2n+1}$ is neither of the forms $x^2 \pm y^2$.

So $V(2) \geqslant 3$. But $v(2) = 3$.

Hence Theorem V is proved.*

* These two proofs owe to the ideas contained in 21·8, Chap. XXI, in *An Introduction to the Theory of Numbers*, by Hardy and Wright.

PIGMENTS OF COTTON FLOWERS

Part VII. Position of the Glucose Residue in Gossypitrin

By P. Suryaprakasa Rao and T. R. Seshadri

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Received March 6, 1939

Gossypitrin which is the most important component of the Indian cotton flowers is a monoglucoside of the flavonol, Gossypetin. It was shown in a previous publication[1] from these laboratories that though the position in which the sugar group is situated could be surmised from various considerations, it has not yet been definitely established. An attempt described in the above paper to settle this question by methylating Gossypitrin with diazomethane was not successful since one of the nuclear hydroxyls (probably the one in position 5) was resistant to methylation by this reagent. The partially methylated Gossypitrin on hydrolysis produced a new compound which was tentatively given the constitution of 3′ : 4′ : 3 : 8-tetramethyl gossypetin.

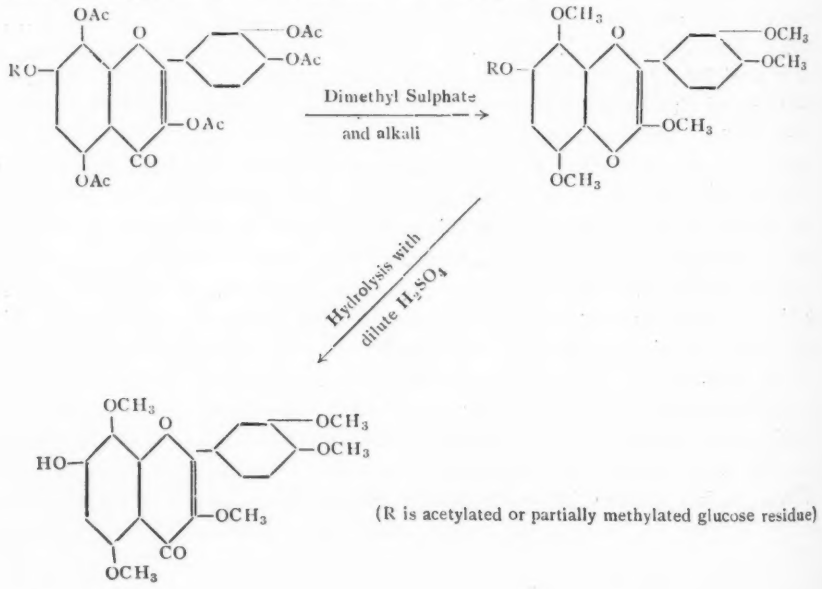
Methylation of the glucoside using alkali and dimethyl sulphate or methyl iodide was not feasible since the pigment is highly sensitive in the presence of alkali and readily undergoes oxidation. Amongst the other possible methods, utilisation of the acetyl derivative as the starting material seemed to be worth trial. This method was employed by Freudenberg and Cohn[2] for preparing the methyl ether of quercetin and subsequently improved by Anderson[3] to obtain better yields. They used a methyl alcoholic solution of the acetyl derivative and methylated it with dimethyl sulphate and alkali. The completely methylated compound was not the exclusive product ; the partially methylated tetramethyl ether was also obtained in considerable amounts. We have now found that the substitution of acetone for methyl alcohol as the solvent effects considerable improvement in yielding the completely methylated ether exclusively. The superiority of acetone over methyl alcohol is due to its specific influence in the methylation of the hydroxyl group in position 5 as was observed by Baker and Robinson.[4] We have applied this method for the methylation of Gossypitrin through its acetyl derivative. Though the acetate is rather sparingly soluble in alcohol it dissolves more easily in acetone. The product undergoes deacetylation and methylation smoothly. All the phenolic hydroxyl groups and one hydroxyl in the sugar residue are methylated by this process. On hydrolysis with dilute sulphuric acid, this methylated glucoside gives rise to a pentamethyl

gossypetin which agrees in all its properties with 3 : 5 : 8 : 3′ : 4′-pentamethyl gossypetin obtained by Baker, Nodzu and Robinson[5] during the course of the synthesis of gossypetin.

	3 : 5 : 8 : 3′ . 4′-pentamethyl gossypetin	The pentamethyl gossypetin obtained by the hydrolysis of the methylated glucoside
Melting point	253–54°	252–54°
Colour with ferric chloride	No characteristic colour	No characteristic colour
Solubility in sodium hydroxide	Easily soluble to give yellow solution	Easily soluble to give yellow solution
Solubility in concentrated HCl	Soluble to give yellow solution	Soluble to give yellow solution
M.P. of the acetyl derivative	....	167-69°

On boiling with acetic anhydride and anhydrous sodium acetate the pentamethyl gossypetin gives rise to the monoacetate of the pentamethyl ether. On further methylation with dimethyl sulphate and alkali, it yields the hexamethyl gossypetin.

It is therefore concluded that the hydroxyl group in position 7 of the aglucone which has been left free at the end of the methylation and subsequent hydrolysis of the glucoside is involved in the glucoside formation. Hence Gossypitrin is a 7-glucoside of Gossypetin.



(R is acetylated or partially methylated glucose residue)

Experimental

Gossypitrin acetate (3 g.) was dissolved in acetone (120 c.c.) and dimethyl sulphate (30 c.c.) and 20% aqueous sodium hydroxide (30 c.c.) were added to the solution. On shaking, the contents assumed a lemon yellow colour which faded away gradually. Thereupon more quantities of methyl sulphate (15 c.c.) and 20% sodium hydroxide (15 c.c.) were added alternately in small amounts using 3 c.c. each time and shaking vigorously after each addition. Finally the medium was kept definitely alkaline by the gradual addition of 30 c.c. more of the above alkali. There was gradual development of heat throughout the process and during the later stages the mixture became so hot that there was actual boiling. After leaving overnight it was gently boiled under reflux on a water-bath for an hour. Then almost all the solvent was driven off. At this stage the methylated glucoside separated out as a crystalline solid on cooling. But sometimes the contents deposited a small amount of a brown coloured pasty mass along with the beautifully crystalline solid. In such cases the supernatant liquid was decanted off and the residue treated with a small amount of ether when it changed into a colourless crystalline solid. The decanted liquid deposited some more of the same substance. The methylated glucoside was then crystallised twice from acetic acid and was obtained as tiny needles which were almost colourless. It melted at 290° with decomposition, becoming dark a few degrees earlier. [Found : OCH_3, 31·8 ; $C_{21}H_{14}O_7$ $(OCH_3)_6$, H_2O requires OCH_3, 32·0%.]

The above methylated glucoside (1 g.) was boiled under reflux with 7% sulphuric acid (100 c.c.) when it went into solution. After an hour a faintly coloured solid separated out giving rise to slight bumping. Boiling was continued for one hour more to ensure complete hydrolysis of the glucoside. The pale yellow solid which separated out on cooling the contents was filtered and then crystallised from alcohol using a little animal charcoal. The product came out in the form of fine golden yellow needles melting at 252–54°. It dissolved in hydrochloric acid and sodium hydroxide to form yellow solutions. It imparted no characteristic colour to ferric chloride in alcoholic solution. [Found : C, 61·6 ; H, 5·1 ; OCH_3 39·7 ; $C_{15}H_5O_3$ $(OCH_3)_5$ requires C, 61·9, H, 5·2, OCH_3, 40·0%.]

7-Acetyl-3 : 5 : 8 : 3′ : 4′-pentamethyl gossypetin.—The above pentamethyl ether (100 mg.) was boiled under reflux with anhydrous sodium acetate (1 g.) and acetic anhydride (20 c.c.) for 4 hours. On diluting the contents with 200 c.c. of cold water and leaving overnight, a colourless fibrous solid separated out. It was obtained as a hydrate in the form of fine needles,

when crystallised from alcohol or acetic acid. It sintered from 100 to 105° (dehydration) and melted completely at 167–69°. It lost all the water of crystallisation when kept at 125° for 2 hours. [Found : OCH_3, 32·8 ; loss of H_2O on drying, 10·8 ; $C_{15}H_4O_2$ (CH_3 COO) $(OCH_3)_5$, $3H_2O$ requires OCH_3 32·0 ; loss on drying, 11·2%.]

3 : 5 : 7 : 8 : 3′ : 4′-*Hexamethyl gossypetin*.—The above pentamethyl gossypetin when methylated with dimethyl sulphate and alkali yielded the hexamethyl ether. Addition of some methyl alcohol was helpful in getting a clear solution and in obtaining a good yield. The hexamethyl gossypetin crystallised from alcohol as colourless fibrous needles melting at 170–72°.

Summary

The constitution of Gossypitrin has been established as the 7-glucoside of the flavonol Gossypetin by complete methylation of the glucoside through the acetyl derivative and the isolation of 7-hydroxy-3 : 5 : 8 : 3′ : 4′-pentamethoxyflavone by the hydrolysis of the above methylated glucoside. The acetyl derivative of the pentamethyl gossypetin has also been prepared.

Our thanks are due to Dr. S. Rangaswami for help in connection with the microanalysis of the compounds.

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THE MAGNETIC SUSCEPTIBILITY OF MERCURY AND OF SOME DILUTE ALKALI AMALGAMS

By S. Ramachandra Rao and S. Aravamuthachari
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Received February 28, 1939

1. Introduction

The problem of the nature of the alkali amalgams has been investigated by a large number of workers. Most of the work on the physical properties of alkali amalgams has been directed towards the elucidation of the state of the alkali elements in the amalgams.

Perhaps the earliest investigations in this direction were carried out by Kerp (1898) who determined the exact solubility of the alkali elements in mercury. In a latter paper, Kerp and Bottger (1900) determined at various temperatures the composition of each of the solid phases in equilibrium and advanced the idea of the probable existence of definite compounds between the alkali elements in solution and mercury.

More accurate work on such lines was carried out by Smith and Bennett (1910) by preparing solid crystals of the alkali amalgam by the electrolytic method. The amalgam crystals were separated by filtration and any adhering mother liquor was removed by means of a high-speed electric centrifuge machine. The crystals were at once analysed by being dissolved in excess of 0·1 N hydrochloric acid. After decomposition of the amalgam, the contents were titrated back with 0·1 N sodium hydroxide. The alkali content of the amalgam was thus calculated from the volume of the acid that was required to actually decompose the amalgam. Their results indicate the existence of compounds of the formula $CsHg_{12}$, $RbHg_{12}$, KHg_{12}, $NaHg_5$ and $LiHg_3$. They consider the conclusions regarding sodium and lithium as quite reliable.

They have also determined the weight of the amalgamated metal present in 100 grams of the saturated liquid amalgam. These metals are not present in the solution in the free state : they are present in the form of compounds of the general formula $MeHg_n$ where Me corresponds to one atom of the dissolved metal and n is a number not exceeding 12.

Richards and Conant (1922) studied the electrochemical behaviour of liquid amalgams of sodium and found that the deviations from the simple

concentration law were larger in the case of sodium amalgams than with any other mercurial solution studied by them. They are inclined to attribute this property to the hydrargyration of the dissolved sodium.

A reference must be made to the interesting conclusions of Lewis, Adams and Lanman (1915). They found that when an electrical current was passed through a dilute amalgam of sodium or potassium, a transfer of the dissolved metal in the direction of the negative current took place. They have pictured a dilute amalgam as composed of small regions whose centres are the alkali atoms, embedded in a mass which has all the properties of pure mercury. During the passage of an electrical current, an electron meeting one of these regions is retarded. By the law of actions and reactions, the region containing the sodium atom is impelled in the direction of the negative current. One can realise that this picture can never be true for the masses of the aggregates are large when compared with that of the electron. But the point which requires mention is that Lewis and others do not refer to any chemical compounds in the dilute amalgam but speak only of loose associations.

Evidence for the formation of compounds even in dilute amalgams is furnished by the investigations of Bent and Hildebrand (1927) on the vapour pressures of sodium and cæsium amalgams. The whole of the deviation from perfect solution exhibited by sodium amalgams can be explained on the assumption of the formation of $NaHg_2$, $NaHg_4$ and $NaHg_6$. In very dilute amalgams, the compound $NaHg_{16}$ appears to explain both vapour pressure and electromotive force data. However, similar investigations of the vapour pressures of potassium amalgam by Millar (1927) have not led to any definite compounds of the form $MeHg_n$.

Bhatnagar, Mata Prasad and Mukherji (1924) have determined the surface tension of sodium and potassium amalgams at the amalgam-benzene interface. The amalgams were prepared by the electrolytic method. The interfacial tension was determined by the drop method. In the graph between concentration and surface tension, two discontinuities were obtained in the case of each amalgam. The concentrations by weight at which discontinuities were observed were 0·06 per cent. and (about) 0·28 in the case of sodium amalgam and 0·08 per cent. and (about) 0·16 in the case of potassium amalgam. The authors have attributed this variation to the formation of compounds of sodium and potassium with mercury at very low concentrations of the alkali metal. At other concentrations studied (below 0·312 per cent. for sodium and 0·182 per cent. for potassium), the amalgam is supposed to be a solution of the compounds and the solid metal in mercury.

The electrical conductivity of alkali amalgams has also been the subject of study by a large number of investigators. Bornemann and Muller (1910)

showed that the electrical conductivity of mercury was lowered by the addition of sodium. Vanstone (1914) studied the specific volume and electrical conductivity of amalgams rich in sodium. Hine (1917) investigated the electrical conductivity of dilute sodium, lithium and potassium amalgams. In the case of sodium, the resistance of the amalgam at first increased with increase of sodium concentration ; a maximum resistance was obtained at a concentration of nearly 2·4 atoms per cent. and the resistance gradually diminished at higher concentrations. For lithium amalgams, the resistance decreased uniformly as the concentration of lithium was increased up to 0·82 atom per cent. When, on the other hand, potassium is added to mercury, the resistance of the amalgam increases comparatively rapidly in the range of concentration (1·186 atom per cent. of potassium) studied. These measurements show a striking difference in the effect of the metal added to mercury for metals of such general similarity. Other metals added to mercury lower the resistance and sodium and potassium behave differently in their influence on the conductivity of mercury.

The electrical conductivity of dilute amalgams of lithium, sodium and potassium were also investigated by Boohariwala, Paranjpe and Mata Prasad (1929). Their concentration-conductivity curves resemble the concentration-surface tension curves of Bhatnagar, Mata Prasad and Mukherji (1924) and the discontinuities obtained by them occur at about the same concentrations as those obtained by the latter authors. These results however are not in agreement with those of Hine (1917).

A careful investigation on the conductivity of dilute amalgams at different temperatures between 0° C. and 302·2° C. was carried out by Davies and Evans (1930). Their results are in substantial agreement with those of Feninger (1914) and Hine (1917). They had previously studied the amalgams of metals belonging to groups II, III and IV of the periodic table. They have shown definitely that while generally solutions of metals in mercury cause an increase in conductivity, sodium produces a definite decrease. Attention has been drawn to the evolution of heat during the solution of the alkali elements in mercury and also to the fact that the viscosity of the alkali amalgams is greater than that of the amalgams of other metals.

It is relevant to mention here that Paranjpe and Joshi (1932) have produced a large amount of evidence to show that liquid sodium amalgams are hydrargyophilic colloidal solutions of sodium in mercury with $(Na_x)\ Hg_y$ as the colloidal micellæ. They are of opinion that the properties of a dilute amalgam depend on the method of preparation, the age and the previous history of the sample.

Bent (1933), however, has advanced fairly convincing views that this conclusion of Paranjpe and Joshi (1932) is not supported by experimental evidence. Attention is drawn to the following facts, which either prove or constitute strong evidence, that sodium amalgams are true solutions: (*a*) the freezing point depression of mercury in dilute amalgams is that calculated for an ideal solution (*b*) the vapour pressure lowering is that calculated for an ideal solution. In more concentrated amalgams, the lowering is greater than is calculated for an ideal solution. A colloidal solution should have a smaller lowering of the vapour pressure.

These details are presented at some length to show the complexity of the problem. While various physical properties of dilute alkali amalgams have been studied, the magnetic susceptibility of the amalgams does not seem to have been studied before. The change of magnetic susceptibility of mercury brought about by the addition of small quantities of the alkali elements is bound to throw much light on the nature of dilute alkali amalgam. The present work was undertaken with this purpose in view. The subject is also of interest from the purely physical standpoint relating to the theory of electrical conduction in metals. The resistance of metals shows a relatively large increase due to small amounts of impurities in solid solution. Liquid mercury is anomalous in that the solution of most other metals in it decreases the resistance. But sodium and potassium dissolved in small quantities in mercury increase its resistance.

Mercury is also anomalous from another point of view. The increase in its resistance when it is converted from the solid state into the liquid state is exceptionally large. This has been attributed by Mott and Jones (1936, p. 278) to the change in the crystal structure, the mean interatomic distance in liquid mercury corresponding to a close-packed structure while the solid is rhombohedral. It is interesting to draw attention also to the fact that the alkali metals show an increase of resistance on melting. One would expect the resistance to be unaltered since the effective number of free electrons remains unaltered. The change of resistance observed is attributed by Mott and Jones (1936, p. 277) to the increased disorder in the liquid phase.

The magnetic susceptibilities of dilute amalgams of gold, tin, indium and gallium were determined with the aid of a Curie-Cheneveau magnetic balance by Davies and Keeping (1929). The diamagnetic susceptibility was found to decrease in absolute value as the concentration of the dissolved metal was increased but not linearly. The effect per atom added on the susceptibility of mercury was greater in the case of indium than that in the case of other metals. In the case of gold, the decrease became linear between concentrations of 0·1 and 0·25 per cent. by weight.

Bhatnagar and Mathur (1935, p. 341) have stated that dilute copper amalgams are merely mechanical mixtures of the two metals and that the value of the magnetic susceptibility varies from that of pure mercury to that for pure copper.

Bates and Tai (1936) investigated the magnetic susceptibilities of a series of dilute amalgams of known concentrations of bismuth, chromium, copper and manganese. In the case of copper amalgams, the specific diamagnetic susceptibility showed a decrease as the concentration of copper was increased. No linear relation was obtained indicating the presence of mere mechanical mixtures of copper and mercury. An abrupt increase of slope was noticed by them at a concentration of nearly 3 per cent. by weight of copper. All the metals studied by them (which are diamagnetic in the solid state) were found to be paramagnetic in dilute amalgams, with the possible exception of copper.

Bates and Tai (1937) investigated the magnetic properties of manganese amalgams. Bates and Illsley (1937) studied iron amalgams. Bates and Ireland (1937) examined dilute amalgams of silver. Unlike gold and copper, silver was found to increase the specific diamagnetic susceptibility of mercury.

The susceptibility of dilute alkali amalgams does not seem to have been studied before and a careful determination of the changes produced in the specific susceptibility of mercury by small quantities of alkali elements seemed profitable from the physical point of view also.

2. *Experimental*

(*a*) *Purification of mercury.*—The available mercury was a sample from Kahlbaum marked ' for analysis '. Further purification was effected in two ways. The results obtained by the two methods however showed that the initial sample available for work was an exceedingly pure specimen.

The first method was that of Hulett (1911). The apparatus used is shown in Fig. 1. Mercury is poured into the tube A connected at the top to a narrower tube. The mouth is widened out a little and a tube B is inserted. A rubber band cut from a rubber tubing of suitable diameter slipped over the junction makes the connection air-tight. A bulb is blown in the middle of B to fit the mouth of A. The lower end of B is drawn into a fine capillary. At the upper end is sealed a tube containing a grease-free well-ground stop-cock.

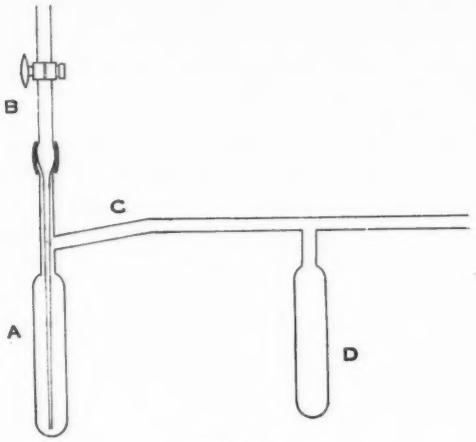

FIG. 1

A side tube C is attached to A. To this side tube is connected a wide tube D immersed in a mixture of ice and salt. C is connected to a hyvac pump.

The bulb A is placed on a sand-bath heated from below by a Bunsen burner. The hyvac pump is kept working and the stop-cock is adjusted so that air bubbles into the mercury through the capillary. The pressure inside is arranged to be about 2·5 cm. of mercury. The mercury distils over into the bulb D. When a small quantity of mercury is still left in A, the stop-cock is closed. When the pressure is reduced to the lowest value possible the tube D is sealed off at the constriction. It is kept aside till the mercury inside is to be used.

The effect of successive distillation of mercury was also studied carefully. The apparatus used is shown in Fig. 2. Mercury distilled in vacuum was poured in bulb A, the first of five bulbs connected as shown in Fig. 2. The inlet was sealed off at the place *a*. The free end at the top was connected to a vacuum outfit consisting of a Waran pump backed by a Cenco-Hyvac pump and a Macleod guage. By working the pumps, the pressure was brought down to the order of 10^{-4} cm. By gently warming the mercury in A, it was made to distil in B. When nearly 4/5 of the volume was evaporated, the connecting tube was sealed off at *b*. In a similar manner, mercury was distilled successively into the bulbs, B, C, D and E and the connecting tubes were sealed off at *c*, *d*, *e* and *f*. Enough mercury was left in each bulb for magnetic investigations.

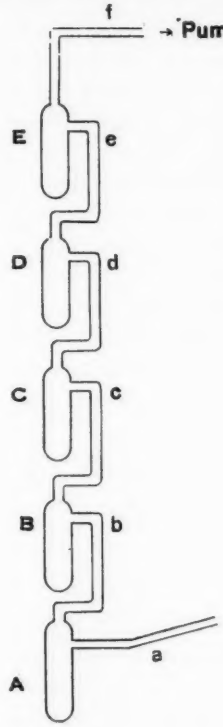

FIG. 2

FIG. 3

The mercury in each bulb was transferred to small bulbs about 4 mm. diameter, blown at the end of thin-walled glass tubes. These bulbs were sealed *in vacuo* after keeping the mercury for some time to get it free from occluded gases if any and were studied by the Curie method.

(*b*) *Purification of the alkali elements.*—The magnetic susceptibility of alkali elements had to be determined in the pure state and also in the state of solution in mercury.

To prepare them in the pure state for purposes of magnetic investigation, the following method was adopted. A pyrex tube having a diameter of about 6 mm. was drawn in the shape shown in Fig. 3. A bulb was blown at one end E. After thoroughly drying the tube (after connecting it to the pump and heating strongly) a suitable amount of freshly cut sodium immersed in benzene was introduced at A and the end connected by a short length of pressure tubing to the vacuum outfit. The pressure was quickly

reduced to a value slightly lower than 10^{-4} cm. With a Bunsen burner, the whole tube AE was uniformly warmed to and fro keeping the tube inclined to the vertical at an angle of nearly 45°. Then the upper part of the tube in the region A was heated to melt the sodium and prevent its evaporation into the pump side. The vapour of the metal descended into the cooler part of the tube B and condensed there. By suitable manipulation, the metal was condensed successively into C and D and finally in E. The stop-cock in the connection from A to the pumps was kept closed during the experiment and was opened now and then to remove any occluded gases.

When a suitable quantity of sodium was collected in the bulb E, the tube was sealed off at *e* and the molten glass was drawn to give a hook for the bulb to be suspended during the magnetic investigations.

This method was very conveniently used for preparing pure specimens of sodium, potassium and rubidium. About 0·1 gram was the mass of the metal usually collected in the bulbs.

(*c*) *Preparation of the amalgams.*—The four methods by which alkali amalgams are usually prepared are: (1) directly from metals, (2) by the action of an amalgam on a salt solution, (3) by the electrolysis of a complex alkali-mercury salt in aqueous solution with platinum electrodes, (4) by the electrolysis of a salt solution with a mercury cathode.

In this investigation the amalgams had to be dilute and very pure. The concentrations of the alakli element had to be less than 3 per cent. After a careful consideration of the relative advantages of the different methods, it was decided to prepare the amalgams by the first method. It is the simplest method and the component elements have no chance of coming into contact with air or any other extraneous substance.

Two methods of preparing the amalgams were employed. The apparatus used in the first method is shown in Fig. 4 and was made of pyrex.

A suitable amount of previously distilled mercury was taken in D. A small quantity of sodium was placed in the tube A. The open end A was connected to a small length of pressure tubing made of India rubber closed at the upper end with a short glass rod. By connecting the end *c* to the pump equipment, the pressure was rapidly reduced to less than 10^{-4} cm. With the help of oxygen-kerosene gas flame, the tube A was closed just below the rubber connection.

The mercury was gently warmed to remove occluded gases if any and then heated uniformly to make it evaporate and condense in C. When a suitable quantity had collected in C, the constriction at *b* was sealed and D was removed.

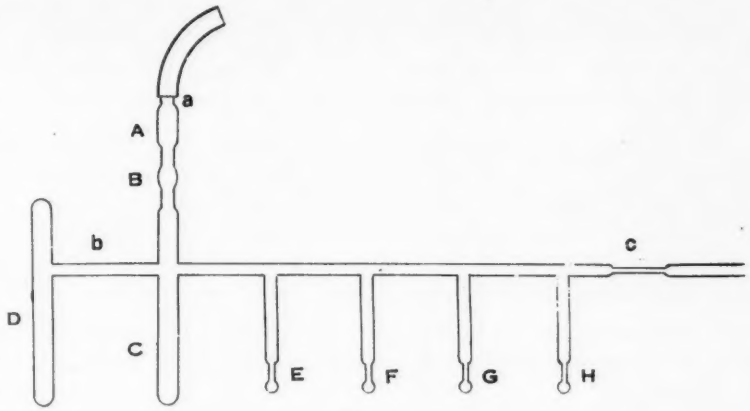

FIG. 4

The sodium in A was next warmed and made to condense in the bulb B. By heating A and B, it was next made to condense in the upper part of C. When a suitable quantity of the silvery white metal had collected in C, the constriction between B and C was sealed off and the upper part was removed. The whole tube *c* was gently warmed and since the free end C was connected to the vacuum equipment with pressure tubing, the tube could be shaken briskly to bring together the sodium and mercury. Since the amount of sodium used for the amalgam was small, the amount of heat produced during the mixing was not considerable.

The outlet tube was then sealed off at C. The amalgam was next transferred in small quantities to the bulbs E, F, G and H. These bulbs were next sealed off one after another.

This method was used also for preparing potassium amalgams. The magnetic susceptibility of different specimens taken from the same amalgam could thus be studied.

The amalgam in each of the four bulbs and in the tube C were analysed to determine the alkali content.

The amalgams were also prepared with the tube shown in Fig. 3. A suitable amount of mercury (about 0·35 g.) was taken initially in the bulb E. A small piece of sodium was inserted at the open end A which was then connected to the high vacuum outfit. The mercury was first heated to drive out any occluded gas. The tube was shaken now and then to make any mercury condensed in the part D to run down. The sodium was next heated and as was explained in part (*b*) above, it was successively distilled into B, C and D. By suitably inclining the tube the mercury was run into

D and if the mercury was warm initially, the amalgam was quickly formed. The sides of the tube at D were now clear having been cleaned of the alkali metal by mercury. The amalgam was then run back into the bulb E. The narrow connection *e* between the bulb and the part D was sealed off.

This method was adopted for preparing amalgams of lithium, sodium, potassium and rubidium. In the case of lithium, the metal was distilled only once, the parts B and C being omitted from the tube shown in Fig. 3. This was because it took a comparatively long time for a sufficient amount of lithium vapour to be condensed. The amalgams were thus prepared completely in vacuum and were consequently very pure specimens.

(*d*) *Determination of magnetic susceptibility.*—The magnetic susceptibilities of the pure elements and of the amalgams were determined by the Curie method.

The current for the electromagnet was supplied by a 120 volt generator steadied by a battery of 60 accumulators. With the aid of rheostats, the current in the circuit should be varied from 3 to 7 amperes. A commutator was employed to reverse the current in the electromagnet. The currents were measured with an ammeter of the Cambridge Scientific Company reading accurately to 0·05 ampere and by estimation to 0·005 ampere. The deflections of the spot of light on the scale were read.

The retorsion method was adopted, the bulb containing the specimens under investigations being brought with the help of the torsion head to the same position to within 1 cm. on the scale in the presence of the magnetic field. On switching off the current, the deflection of the spot of light was read on the scale.

The bulb was arranged to lie between the pole faces in such a manner that its image when seen through a telescope was symmetrical around the point of intersection of the cross wires.

The standard substance used was water, the specific susceptibility of which was assumed to be $-0{\cdot}720$* at 30° C.

After finding the deflection corresponding to the bulb, it was weighed and broken open. In the case of mercury, it was thrown out and the deflection corresponding to the empty bulb was found. When the bulb contained alakali metal or amalgam, the contents were removed as detailed in the next section. The bulb was dried in a vacuum desiccator and its deflection obtained by the magnetic method.

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* Susceptibility values in this paper are given in 10^{-6} units.

If d_s and d_w be the deflections obtained for the substance and water respectively, it may be shown that

$$\frac{d_s}{d_w} = \frac{k_s v_s - k_a v_i}{k_w v_w - k_a v_i'},$$

where k_s and k_w are the volume susceptibilities of the substance and water respectively, v_s and v_w their volumes, k_a the volume susceptibility of the surrounding air and v_i and v_i' the internal volumes of the bulbs containing the substance and water.

If m_s, m_w and χ_s, χ_w are the masses and specific susceptibilities of the substance and water respectively, we obtain

$$\frac{d_s}{d_w} = \frac{m_s\chi_s - k_a v_i}{m_w\chi_w - k_a v_i'}.$$

The volume susceptibility of air at N. T. P. is $+0{\cdot}029$ (*Int. Crit. Tables*, 1929). Remembering that for a paramagnetic gas, the volume susceptibility varies directly as the square of the absolute temperature, the volume susceptibility at atmospheric pressure and at 30° C. is found to be $0{\cdot}036$. The bulbs prepared had an internal diameter of nearly 4 mm. which gives for the internal volume a value of about $0{\cdot}032$ c.c. Hence $k_i v_i$ becomes $0{\cdot}036 \times 10^{-6} \times 0{\cdot}032$ or $0{\cdot}00115 \times 10^{-6}$.

For measurements with mercury and the amalgams, the usual mass taken was nearly $0{\cdot}35$ g. The specific susceptibility being about $-0{\cdot}16$, m_s becomes $0{\cdot}16 \times 10^{-6} \times 0{\cdot}35$ or $0{\cdot}056$.

Since the deflections d_s and d_w are arranged to be nearly equal, $m_w\chi_w$ is nearly equal to $m_s\chi_s$ or $0{\cdot}056$.

A rough calculation shows that not much error is committed by neglecting the susceptibility of air. Hence

$$\frac{d_s}{d_w} = \frac{m_s\chi_s}{m_w\chi_w}$$

$$\text{or } \chi_s = \frac{m_w}{m_s} \cdot \frac{d_s}{d_w} \cdot \chi_w.$$

But in determining the specific susceptibility of the pure alkali metals $m_s\chi_s$ is not so large as in the case of mercury or the amalgams. Hence the internal volumes of the bulbs were determined by filling them with water and weighing; and the correction for the susceptibility of air was applied in the calculation of the susceptibility of the alakli metal.

It must be added that by blowing bulbs with thin walls, the weights of the bulbs were made as small as possible and thus the deflections due to them were small compared with the deflections due to the substances inside them.

The error in the values of the susceptibility in the following measurements does not exceed 1/2 per cent.

Correction for the presence of ferromagnetic impurities.—It is well known that the presence of even small traces of ferromagnetic impurities affect the magnetic susceptibility of substances profoundly.

A careful test was made for any such impurities that might be present in the substances studied. This was effected by determining the susceptibility in every case at five different field currents, *viz.*, 3, 4, 5, 6 and 7 amperes. The field strength varied in this range from about 3 to 7 kilogauss.

If χ_p and χ_i are the specific susceptibilities of the pure and impure samples of any substance, according to Honda (1910) $\chi_p = \chi_i + \frac{\sigma m}{H}$, where σ is the specific intensity of magnetisation of the impurity, m the mass of the impurity in unit mass of the substance and H the field intensity.

If the specific susceptibility remains constant at different field strengths, there is no ferromagnetic impurity in the substance. If, however, the specific susceptibility χ_i varies with H, it follows that there is a small quantity of the impurity. In such a case a graph is drawn between χ_i and 1/H. The points plot themselves on a straight line. On producing this straight line to meet the Y axis, the value of the specific susceptibility when $1/H = 0$ or $H = \infty$ is obtained. This specific susceptibility measures the value of the pure specimen for when $1/H = 0$, $\chi_p = \chi_i$.

(*e*) *Determination of the alkali content in the amalgam.*—After the magnetic measurements, each bulb was weighed in a chemical balance accurate to 1/10 of a milligram and cut open. The opened bulb was dropped into a freshly steamed hard glass flask containing about 20 c.c. of conductivity water. Special conductivity water had to be used in place of ordinary distilled water since the latter was slightly alkaline and hence interfered with the titration values, particularly since small quantities of the alkali elements had to be estimated. The conductivity water was freshly prepared and thoroughly boiled to expel any dissolved gases including carbon dioxide.

After dropping the bulb in the conductivity water, the container was heated to nearly the boiling point of water. The estimation of the alkali element was carried out in accordance with the improved procedure for alkalimetric titration given by Lewis, Adams and Lanman (1915). About 2 c.c. of a solution (0·1 per cent.) of rosalic acid in conductivity water was added to the contents of the flask. 1 c.c. of N/10 hydrochloric acid, standardized against pure sodium carbonate, was added with the aid of a 1 c.c. pipette

graduated to 0·01 c.c. The solution which was pink initially now turned yellow. In the case where the alkali content was relatively larger, as much acid was added as was necessary to turn the colour from pink to yellow. The amount of acid added was adjusted to be much in excess of the amount just required to neutralise the alkali hydroxide in the solution.

The excess of acid added was estimated by titration against a N/100 solution of sodium hydroxide free from sodium carbonate. From this it was possible to determine the exact volume of N/10 hydrochloric acid necessary to neutralise the alkali hydroxide initially produced from the amalgam. The concentration of this hydroxide, being thus estimated, it was easy to calculate the percentage of the alkali element in the amalgam.

The N/100 solution of sodium hydroxide used for titration against the excess acid was prepared from sodium metal by the action of water upon it in an atmosphere free from carbon dioxide. The solution obtained by this process was very concentrated and had to be diluted to the required concentration.

The burette used for the titration was of 10 c.c. capacity and was divided into 1/50 c.c. The volumes could therefore be read to 0·02 c.c. and by estimation to 0·01 c.c.

It was essential to keep the standard solution of sodium hydroxide free from atmospheric carbon dioxide since the indicator used fades appreciably in the presence of carbon dioxide. To enable this precaution to be adopted, the burette used was of the Baryta type.

Another precaution which had necessarily to be taken is to free the solution from absorption of carbon dioxide from the atmosphere during titration. When only a slight excess of acid remained, a stream of air freed from carbon dioxide by soda lime, was led through a glass tube into the solution. This was effective not only in stirring the solution, but also in completely sweeping out whatever carbon dioxide might be dissolved. The end point was then very sharply obtained.

Considering the sources of error likely to arise in these determinations it may be mentioned that the estimations of the alkali metal in the amalgam are correct to within 1 per cent. Check measurements were made by dissolving known weights of pure alkali metals in water and determining the alkali content by the above method. In all cases, the gravimetric and the volumetric estimations agreed to within one per cent.

3. Results

(*a*) *Susceptibility of mercury.*—Measurements of the magnetic susceptibility of mercury were made with the Kahlbaum sample for analysis after

filtration through a fine capillary glass tubing. The values obtained with six samples are given below.

TABLE I

Sample No.	Specific susceptibility
1	− 0·164
2	− 0·163
3	− 0·165
4	− 0·164
5	− 0·164
6	− 0·165
Average	− 0·164

For each sample, the specific susceptibility was determined at field currents of 3, 4, 5, 6 and 7 amperes. These results showed a trace of ferromagnetic impurity. Hence for each sample, the specific susceptibility was obtained by drawing a graph between χ and 1/H. By extrapolating it the susceptibility when $1/H = 0$ was found.

Next the mercury prepared by the Hulett method was studied. Bates and Baker (1938) have made a careful investigation of the purification and magnetic properties of mercury. They prepared pure mercury by the Hulett method and found that the differences between the magnetic susceptibility of several specimens were removed completely by heating the mercury *in vacuo* at 260° C. for some time.

The same procedure was adopted in the present investigation. Six samples were studied and each sample was heated in *vacuo* in the pyrex bulb before being sealed in. Mercury treated by this method showed no trace of ferromagnetic impurity. The specific susceptibility was independent of the field strength. The average of six samples gave a value of 0·1662.

The effect of successive distillation *in vacuo* on the specific susceptibility of mercury was also studied as detailed in Art. 2 (*a*). The results are given below. The average value obtained with three bulbs is given for each specimen.

TABLE II

Number of successive distillations	Specific susceptibility
1	− 0·1642
2	− 0·1663
3	− 0·1657
4	− 0·1661
5	− 0·1659

An examination of Table II shows that the specific susceptibility practically attains a steady value after the second distillation. The ferromagnetic impurity disappeared even after the first distillation.

Freshly prepared mercury which showed a susceptibility value of 0·1659 was placed in a pyrex tube with its mouth drawn into a fine long capillary. The mercury was thus in contact with atmospheric air but was free from dust. After a fortnight the specific susceptibility of the mercury had fallen to − 0·1649.

For the preparation of the amalgams freshly prepared mercury after three successive distillations in vacuum was used. The specific susceptibility of the mercury was 0·1660 which agrees closely with the specimens prepared by the Hulett method. The values obtained with pure mercury are given in Table III.

It will be observed that the specific susceptibility obtained in this investigation agrees closely with the values obtained by Vogt and Bates and his associates.

Shur (1937) obtained for the atomic susceptibility of mercury in the vapour state value of − 78. It is of interest to consider the theoretical aspects of the susceptibility of mercury ; but this discussion will be taken up later in Art. 4.

(*b*) *Susceptibility of the alkali metals.*—In this investigation, amalgams of lithium, sodium, potassium and rubidium have been studied.

TABLE III. *Mercury*

Authors	Specific susceptibility	Atomic susceptibility
Owen (1912)	− 0·184	− 36·9
Davis and Keeping (1929)	− 0·189	− 37·9
Vogt (1932 and 1935)	− 0·168	− 33·7
Bates and Tai (1936)	− 0·1675	− 33·6
Bates and Baker (1938)	− 0·1675 (at 30° C.)	− 33·6
Bhatnagar and Nevgi (1937) (for purified and distilled mercury)	− 0·157	− 31·5
Bhatnagar and Nevgi (1937) (for mercury obtained from extra-pure compounds) Mean value ..	− 0·172	− 43·5
Present authors (Hulett method)	− 0·1660	− 33·3
do. (Vacuum distillation)	− 0·1660	− 33·3

The lithium metal used had been studied in this laboratory by Rao and Sriraman (1937) who obtained for it a specific susceptibility of + 2·6. The values obtained are given in Table IV.

TABLE IV

Authors	Specific susceptibilities			
	Lithium	Sodium	Potassium	Rubidium
Honda (1910) and Owen (1912)	+ 0·5	+ 0·51	+ 0·40	+ 0·07
Sucksmith (1926)	..	+ 0·59	+ 0·51	+ 0·07
McLennan, Ruedy and Cohen (1927)	..	+ 0·59	+ 0·45	+ 0·17
Lane (1929 and 1930) ..	..	+ 0·65	+ 0·54	+ 0·21
Rao and Sriraman (1937) ..	+ 2·6	..	..	..
Present authors		+ 0·60	+ 0·52	+ 0·16

The values of the specific susceptibility obtained in this investigation agree satisfactorily with those of other investigators.

(*c*) *Lithium amalgams.*—In this investigation, dilute amalgams of lithium, sodium, potassium and rubidium have been studied.

The results obtained with lithium are given in Table V.

TABLE V

Specimen No.	Percentage weight of lithium	Atomic per cent. of lithium	Specific susceptibility
	0	0	− 0·166
1	0·0016	0·046	− 0·168
2	0·0069	0·20	− 0·169
3	0·0078	0·22	− 0·168
4	0·0165	0·47	− 0·160
5	0·0187	0·53	− 0·158
6	0·0320	0·92	− 0·159
7	0·0560	1·60	− 0·161
8	0·085	2·40	− 0·163
9	0·104	2·86	− 0·165
10	0·109	2·91	− 0·165
11	0·128	3·57	− 0·167
12	0·140	3·89	− 0·168
13	0·162	4·48	− 0·168

It is found that as the concentration of lithium in the amalgam is increased, the diamagnetic specific susceptibility at first shows an increase and attains a maximum value at an atomic concentration of about 0·2%. The susceptibility thereafter decreases showing a broad minimum in the neighbourhood of 0·53 atomic per cent. Thereafter the susceptibility shows a small but uniform increase in value.

(*d*) *Sodium amalgams.*—It was explained in Art. 2 (*c*) that sodium amalgams were prepared by two methods. In the first method, the tube illustrated in Fig. 4 was used. Different samples of the same amalgam could be studied by enclosing small portions in separate bulbs and sealing the tubes *in vacuo*.

Sodium amalgams were also prepared with the aid of tubes similar to the one shown in Fig. 3. We shall call these methods I and II. The results are given in Table VI.

TABLE VI

Bulb No.	Method No.	Percentage weight of sodium	Atomic per cent. of sodium	Specific susceptibility
		0	0	− 0·166
1	II	0·035	0·029	− 0·166
2		0·082		− 0·163
3	I	0·088	0·74	− 0·166
4		0·085		− 0·165
5		0·084		− 0·165
6		0·15		− 0·163
7		0·15		− 0·163
8	I	0·14	1·35	− 0·164
9		0·18		− 0·162
10		0·16		− 0·165
11		0·23		− 0·160
12	I	0·22	2·13	− 0·157
13		0·25		− 0·157
14		0·29		− 0·160
15		0·44		− 0·151
16	I	0·44	3·63	− 0·152
17		0·41		− 0·154
18	II	0·53	4·44	− 0·151
19	II	0·55	4·60	− 0·154
20		0·99		− 0·157
21	I	1·00	8·32	− 0·158
22		1·04		− 0·161
23		1·08		− 0·158
24		1·08		− 0·158
25	I	1·12	8·92	− 0·157
26		1·14		− 0·159

As the concentration is increased the specific diamagnetic susceptibility shows a slow fall in value. The decrease becomes comparatively more rapid after a concentration of 0·75 per cent. is reached. A broad minimum is reached in the neighbourhood of 4 atomic per cent. and thereafter the susceptibility increases gradually in the range studied.

(*e*) *Potassium amalgams.*—The results obtained with potassium amalgam are given in Table VII.

TABLE VII

Specimen No.	Percentage weight of potassium	Atomic per cent. of potassium	Specific susceptibility
	0	0	− 0·166
1	0·002	0·010	− 0·164
2	0·005	0·026	− 0·160
3	0·023	0·118	− 0·157
4	0·025	0·128	− 0·157
5	0·043	0·220	− 0·158
6	0·045	0·23	− 0·159
7	0·075	0·38	− 0·164
8	0·108	0·55	− 0·166
9	0·127	0·65	− 0·167
10	0·176	0·90	− 0·168
11	0·478	2·40	− 0·169

It will be observed that the specific diamagnetic susceptibility decreases as the concentration is increased.

This decrease is fairly rapid. A minimum value is obtained at a concentration of 0·12 (atomic per cent.) and at higher concentrations, the susceptibility increases. This increase is rapid up to 0·30 atomic per cent. and slow thereafter.

(*f*) *Rubidium amalgams.*—Table VIII presents the results obtained with rubidium amalgams.

TABLE VIII

Specimen No.	Percentage weight of rubidium	Atomic per cent. of rubidium	Specific susceptibility
	0	0	− 0·166
1	0·0177	0·04	− 0·157
2	0·035	0·08	− 0·157
3	0·092	0·22	− 0·162
4	0·108	0·25	− 0·164
5	0·160	0·38	− 0·166
6	0·297	0·69	− 0·169
7	0·357	0·83	− 0·170
8	0·652	1·52	− 0·172
9	0·731	1·70	− 0·172
10	1·080	2·50	− 0·174

An examination of these results in comparison with those of potassium is of great interest. A very small quantity of rubidium under 0·04 per cent. produces a considerable fall in the specific susceptibility of mercury. At a concentration of nearly 0·06 atomic per cent. the susceptibility value attains a minimum value. Thereafter the susceptibility increases numerically rapidly up to 0·3 per cent. and more slowly at higher concentrations.

The variation of the susceptibility of rubidium amalgams is exactly similar to the variation of potassium amalgams with the concentration.

(*g*) *Presence of ferromagenetic impurities.*—It is of special importance to examine carefully the amount of ferrromagnetic impurities present in the amalgams ; for small traces of such impurities may vitiate the results considerably.

In all our measurements, the magnetic deflections were observed at five field currents, 3, 4, 5, 6 and 7 amperes. At these field currents, the magnetic

field intensity in the space occupied by the test bulbs was determined with a search coil and a ballistic galvanometer. The field strengths at the above currents were 3·2, 4·9, 5·9, 6·5 and 6·9 kilogauss respectively. Graphs between the specific susceptibility (χ) and 1/H (where H is the magnetic field intensity) were drawn for mercury and the alkali elements examined in this investigation. It was observed that in the cases of mercury, lithium and sodium, the susceptibility was independent of H. These metals were therefore free from ferromagnetic impurities. The graphs for potassium and rubidium showed a slight inclination. But the fact that this inclination was small indicated that the ferromagnetic impurity was present in an exceedingly minute quantity. In the amalgams, only small concentrations of potassium and rubidium were taken and hence the amalgams might be assumed to contain a negligible amount of ferromagnetic impurities. All the amalgams of potassium and rubidium which have been studied here exhibited a constant susceptibility value at different field strengths.

We may therefore conclude that all the materials investigated were practically free from iron or such impurities and that the results were consequently free from any influence due to these impurities.

(*h*) *Variation of atomic susceptibility.*—The variation of the susceptibility per gram atom of the amalgams at different concentrations expressed in atoms per cent. is shown in the four cases studied in Fig. 5. The range of concentration

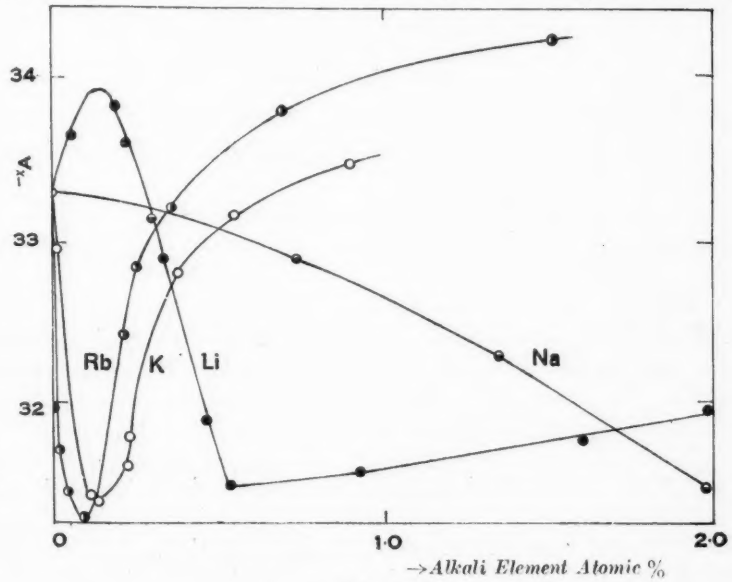

FIG. 5

is between 0 and 1·5 per cent. It is found that at the origion Li shows an increase in the diamagnetic susceptibility; sodium shows a small decrease while potassium and rubidium show a large fall. In the case of lithium the critical points at which inversions take place occur at 0·15 and 0·6 atom concentration. In the case of potassium and rubidium, the minima occur at concentrations of 0·13 and 0·08 respectively. A gradation in the influence of lithium, sodium, potassium and rubidium on the magnetic susceptibility of mercury may be observed when we examine the disposition of the graphs near the origin.

In Fig. 6 the graph for sodium is shown between concentrations of 0 and 10 atomic per cent. A broad minimum is obtained at a concentration of nearly 5 per cent. The significance of this observation will be pointed out in Art. 4.

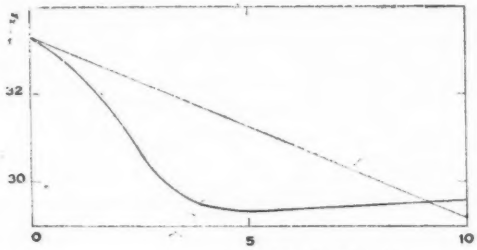

FIG. 6

4. Discussion

(*a*) *The structure of mercury.*—It is essential to consider first of all, the structure of liquid mercury. Let us first examine this problem from the magnetic point of view.

The atomic susceptibility of liquid mercury is found to be $-33·3$. The magnetic susceptibility of mercury vapour has been studied by Shur (1937) who gives the value of -78 as the atomic susceptibility of mercury in the vapour state.

A theoretical calculation of the atomic susceptibility of mercury is possible. The classical formula (see Stoner, 1934, p. 108) for the magnetic susceptibility of a symmetrical atom or ion is

$$\chi = \frac{e}{6mc^2} \Sigma \overline{r}_z$$

where $\overline{r}^2$ is the time average of r^2, r being the distance of the electron from the nucleus. The summation is here extended over all the circumnuclear electrons. e, m and c are the charge on the electron, the mass of the electron and the velocity of light respectively. The factor $\Sigma \overline{r}^2$ has been considered at length

by Slater (1930) who deduced an expression for the susceptibility of an electron in any group.

It is well known that all atoms in the spectroscopic state $^1S_0$ are symmetrical and hence Langevin's formula is applicable in these cases. The mercury atom is $^1S_0$ state (Stoner, 1934, p. 549) and hence the atomic susceptibility may be calculated by Slater's method. A calculation on this basis gives $-84 \cdot 6$ (Bhatnagar and Nevgi, 1937).

These figures clearly indicate that mercury in the vapour state is monoatomic. Since the value in the liquid state ($-33 \cdot 3$) is smaller than the value of mercury in the monoatomic state, it has been suggested (Bhatnagar and Nevgi, 1937) that mercury is polyatomic in the liquid state.

More definite ideas are available from electrical conductivity and crystal structure measurements. The change in the resistance of mercury on melting is exceptionally large. In fact, the ratio of the resistance in the liquid phase to that in the solid phase in the melting point is nearly 4, while in no other metal investigated this ratio is more than $2 \cdot 1$ (Gruneisen, 1928). This fact has been attributed to a change in the crystal structure on melting. Solid mercury has a rhombohedral structure (Wyckoff, 1932, p. 209). X-ray diffraction patterns obtained with liquid mercury by Prins (Randall, 1934, p. 135) definitely indicate a close-packed structure in the liquid. The Bragg spacings in liquid mercury were found to be $2 \cdot 845$ Å, $1 \cdot 41$ Å and $1 \cdot 04$ Å. The band corresponding to the first spacing was most intense.

Menke (1932) using probability considerations, shows a distance rather greater than 3 Å as the most probable separation of neighbouring atoms. Mercury is unique in that no other liquid shows such clear diffraction pattern. That a close-packed structure is present in liquid mercury is now definitely established.

What is the state of the mercury atom in the liquid ? For this question, an excellent answer is supplied by magnetic investigations. Kido (1933) finds for the ionic susceptibility of divalent mercury ion (Hg^{++}) the value of -37. It is surprising that the atomic susceptibility of mercury ($-33 \cdot 3$) falls very near this value. In fact we can go further and identify the difference $+3 \cdot 7$ as the paramagnetic susceptibility of the free electrons associated with a gram atom of mercury.

On the calculations of Pauli (1926) modified by Landau (1930) (for an excellent account see Stoner 1934, pp. 498–505), we obtain for the gram atomic susceptibility of free electrons the expression

$$(\chi_A)_e \times 10^6 = 32 \cdot 11 \frac{q}{V_0},$$

where $(\chi_A)_c$ is the gram atomic susceptibility, q is the number of free electrons per atom and V_0 is the width of the energy band in volts occupied by the free electrons in the completely degenerate state. We obtain for mercury assuming $(\chi_A)_c \times 10^6 = 3 \cdot 7$ and $q = 2$, the value $V_0 = 17 \cdot 4$ volts. Although much emphasis need not be attached to the absolute value of V_0, it is seen that the order of value is near what one would expect for free electrons.

These calculations are made on the assumption that a close-packed crystal structure exists in the liquid mercury. If we consider solid mercury, the atomic susceptibility at $-$ 183° C. is found by Gruneisen and Vogt (Stoner, 1934, p. 512) to be $-$ 23·4 which leads to a value of $+$ 13·6 for the paramagnetic susceptibility of the free electrons in a gram atom of mercury. The width of the energy band in volts occupied by the free electrons becomes therefore $V_0 = \frac{32 \cdot 11 \times q}{(\chi_A)_c \times 10^6} = \frac{32 \cdot 11 \times 2}{13 \cdot 6} = 4 \cdot 7$ volts. The smaller value obtained with the solid mercury indicates the greater freedom of the electrons. This explains satisfactorily the increase of resistance when mercury is converted from the solid phase into the liquid phase.

These considerations give us a definite picture of liquid mercury at laboratory temperatures. A definite crystal structure persists but the unit in which such a structure is present does not seem to have received any attention. From the X-ray or magnetic point of view, mercury exists as ions and the extra-ionic electrons exist almost as free electrons. The regions in which ions exist with a structure may be identified with the polyatomic complexes mentioned by different investigators on mercury.

(*b*) *The influence of compound formation in the range studied.*—There is very little likelihood of any compound formation in the low concentrations studied here. Bent and Hildebrand (1927) suggest the presence of $NaHg_{16}$ even in dilute solutions in the case of sodium amalgams. They mention that the presence of such a compound explains both vapour pressure and electromotive force data. If such a compound is formed, one would expect to get a pronounced change of susceptibility at an atomic concentration of 1/17 or nearly 6 per cent. In this investigation a broad minimum is obtained in the neighbourhood of this concentration. But it remains to be examined whether a compound of the formula $NaHg_{16}$ would give rise to a decrease in the diamagnetic susceptibility of the amalgam.

Assuming the sodium and mercury to exist as monovalent and bivalent ions, the molecular susceptibility of the compound $NaHg_{16}$ may be approximately calculated. The ionic susceptibility of sodium is $= 6 \cdot 1$ according to Hoare and Brindley (1934 and 1935). If the susceptibility contribution of

the free electrons remains unaltered, the molecular susceptibility of $NaHg_{16}$ works to $-31{\cdot}7$. The actual susceptibility obtained at a concentration of nearly 6 atomic per cent. is observed to be $-29{\cdot}3$. Although the values do not agree very much, the direction of variation appears to be the same. The flat minimum in the graph for sodium amalgam may be attributed to the formation of $NaHg_{16}$; but the nature of linkages in this molecule and its structure are still vague and uncertain.

At concentrations below 1 atomic per cent. it is extremely unlikely that compound formation would influence the results even if it obtains in the amalgam. Particularly in the case of potassium and rubidium the variation of susceptibility even at low concentrations is so rapid that compound formation could not account for the change.

(*c*) *Are the alkali atoms in a state of solid solution in mercurry?* A careful examination of the available facts shows that the alkali atoms do not exist in a state of solid solution.

A small amount of foreign matter in solid solution in any metal produces a relatively large increase in the resistance of the metal. Secondly Matthiessen's rule (Mott and Jones, 1936, p. 240) is applicable in the case of solid solution, namely, that the change in the resistance due to a small quantity of foreign metal in solid solution is independent of the temperature.

In the case of dilute amalgams, it is found that the solution of most other metals in mercury decreases the resistance. Hine (1917) has shown that while lithium produces a small decrease of resistance of the corresponding amalgam, sodium and potassium give rise to a small increase of resistance. In no case is the change of resistance large as is required with solid solutions.

Further Bornemann and Rauschenplat (Mellor, 1923, p. 1017) investigated the electrical conductivity of dilute lithium and sodium amalgams at different temperatures between 50° and 300° C. and showed that the specific resistance varied considerably in this range. This is a violation of the Matthiessen's rule and hence electrical conductivity data are definitely against the possible formation of a solid solution of the foreign matter in dilute amalgams.

(*d*) *A probable cause of the observed changes of susceptibility.*—In the study of dilute amalgams of manganese, Bates and Tai (1937) have drawn attention to recent theories regarding the atomic arrangements in alloys put forward by Bragg and Williams (1935) and Bethe (1935). These investigators have supposed that each sort of atoms form on their own a kind of superlattice which repeats itself throughout the specimen, the two lattices existing meshed with each other. The fact that at comparatively small concentrations of the alkali metal, the alkali amalgams become solidified indicates the probable

establishment of such an order. But at very small concentrations, we are probably in the early stages of such an array.

When an exceedingly small quantity of an alkali metal is therefore introduced into mercury, it is likely that it is dispersed into atoms and each atom is surrounded by a group of mercury atoms forming a complex ' molecule ' in a loose sense. The speed with which such an arrangement takes place may give rise to considerable thermal agitation to the atoms of mercury resulting in the development of heat.

It is likely that the initial fall in the diamagnetic susceptibility is due to this cause. When more of the alkali element is added, the alkali atoms join in pairs and a pair of the atoms becomes surrounded by a group of mercury atoms. When this happens, the decrease of diamagnetism would rapidly disappear and the diamagnetism increases rapidly.

If this were true, single atoms of the alkali element dispersed in mercury should possess a high paramagnetic component and double atoms a strongly diamagnetic component. Ample evidence to the former property is borne out by the experiments of Bates and Tai (1936) who find that many metals, which are diamagnetic in the solid state, appear to possess a large paramagnetic component in the amalgam. Also a few metals like manganese which are paramagnetic in the solid state appear to possess nearly 20 times the paramagnetic susceptibility when dissolved in mercury.

That two paramagnetic atoms joining together give a diamagnetic molecule is illustrated by the example of hydrogen.

Potassium and rubidium definitely produce the effects explained above. In the case of sodium, such a rapid initial fall is not observed. Probably the paramagnetic susceptibility of sodium atoms in the extremely disperse condition is only slightly larger than the value for sodium metal. In Fig. 6, the straight line gives the susceptibility values at different concentrations on the basis of the additive law.

Lithium behaves differently from the other alkali elements. The reason seems to be obscure. But it is an offender even in the electrical conductivity measurements. Attention has already been drawn to electrical conductivity measurements by Hine (1917) which show that lithium behaves differently from sodium and potassium. Schmidt (1912) studied the surface tension of very dilute amalgams of the alkali metals. He found that lithium dissolved in small quantities in mercury increased the surface tension of mercury while potassium, rubidium and cæsium diminished its surface tension.

One possible explanation seems to be that the lithium atom is unable to penetrate in the mercury groups as the higher alkali elements do. Probably the lithium atoms stay in the boundary of the groups and penetrate into the mercury groups only when the concentration of lithium is increased.

(*e*) *Influence of change of specific volume.*—Maly (Mellor, 1923, p. 1016) has shown that the specific gravity of alkali amalgams diminishes rapidly even at low concentrations. For example, the addition of 0·6 per cent. by weight of sodium changes the specific gravity from 13·596 to 12·965. This change corresponds to what would have been obtained if the mercury had been heated from 0° C. to 260° C. nearly.

Stoner (1935) has shown that such an increase in volume would be accompained by an increase in the paramagnetic susceptibility component of the free electrons. Hence the specific diamagnetic susceptibility of mercury would decrease.

Bates and Barker (1938) have shown that the specific susceptibility falls from $-0{\cdot}1681$ at 18·5° C. to $-0{\cdot}1637$ at 287·5° C.

At higher concentrations of the sodium in the amalgam the specific volume will be still larger than at 0·6 per cent. Hence due to the expansion in volume alone, the diamagnetic susceptibility would decrease. In the case of sodium, a good part of the decrease in the diamagnetic susceptibility may be attributed to this cause.

We express our indebtedness to Dr. S. V. Anantakrishnan, whose kind co-operation has made this work possible.

Summary

A sample of Kahlbaum mercury marked 'for analysis' was purified by two methods. First the Hulett method of distilling mercury at a low air pressure was adopted. The second method consisted in distilling mercury in vacuum several times. Dilute amalgams of the alkali elements were prepared by mixing pure mercury and the alkali metal after successive distillation in vacuum in pyrex tubes. The amalgams were contained in small pyrex bulbs and the magnetic measurements were carried out by the Curie method. The magnetic susceptibilities of pure sodium, potassium and rubidium have been found. Dilute amalgams of lithium, sodium, potassium and rubidium have also been studied.

The concentrations of the alkali elements in the amalgams were determined by alkalimetric titrations following the improved method of Lewis, Adams and Lanmann.

Samples of mercury prepared by the two methods were found to have nearly the same susceptibility. The atomic susceptibility of mercury in the liquid state is found to be $-33{\cdot}3$. Since the atomic susceptibility of mercury vapour is found to be -78, it is suggested that the mercury atoms exist in the liquid as divalent ions. The valence electrons appear to be free. This conclusion is supported by Kido's value of -37 for the ionic susceptibility of Hg^{++}. Electrical conductivity data suggest that these ions have a close-packed structure in the liquid mercury. It is possible that in the liquid there are large groups of ions each group possessing a close-packed structure X-ray diffraction patterns support this idea.

While at very dilute concentrations of the amalgam, lithium showed an increase of diamagnetic susceptibility, the other alkali metals studied gave a decrease in susceptibility. This behaviour of lithium is analogous with electrical conductivity and surface tension data.

The changes in the susceptibility of mercury due to amalgamation with small quantities of the alkali metals have been examined critically. The influence of compound formation and change of specific volume on the susceptibility is studied. It is suggested that the dispersion of the alkali metal in mercury, in the form of single atoms at very low concentrations and of double atoms at relatively larger concentrations, might explain the observed variation. The atoms of the alkali metals, single or double, appear to be surrounded by groups of mercury ions forming complex molecules. Lithium, however, behaves differently.

Data relating to the other physical properties of very dilute amalgams are considered critically in the light of these considerations.

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A DEFINITE INTEGRAL

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Theorem: *If* n *and* r *are non-negative integers, where* $r < n$, *then*

$$(r+1)\,K(r) = (-1)^{n-1}(n-r)\,K(n-r-1)$$

where

$$K(r) = \int_0^1 \frac{1}{u}(\log u)^r \left\{\log\left(\frac{1+u}{1-u}\right)\right\}^{n-r} du$$

Proof: Integration by parts, gives

$$K(r) = -\int_0^1 \log u \left(\log\frac{1+u}{1-u}\right)^{n-r} \frac{r(\log u)^{r-1}}{u}\,du$$

$$-\int_0^1 (\log u)(\log u)^r \left(\log\frac{1+u}{1-u}\right)^{n-r-1}(n-r)\left(\frac{1-u}{1+u}\right)\frac{2}{(1-u)^2}\,du$$

$$= -r\,K(r) - 2(n-r)\int_1^0 \left(\log\frac{1-x}{1+x}\right)^{r+1}\left(\log\frac{1}{x}\right)^{n-r-1}\frac{(1+x)^2}{4x}\left(\frac{-2}{(1+x)^2}\right)dx$$

by means of the substitution $u = \dfrac{1-x}{1+x}$.

Hence

$$K(r) = -r\,K(r) - (-1)^n (n-r)\,K(n-r-1)$$

Corollary. If n is an even positive integer, then

$$\int_0^1 \frac{1}{u}\left[\left\{\log u + \log\frac{1+u}{1-u}\right\}^n - (\log u)^n\right] du = 0.$$

(See *American Mathematical Monthly*, November 1938.)

Correction to a previous paper. My paper "A remark on $g(n)$" in these *Proceedings* for January 1939 contains some trivial blunders, but the whole argument is rendered correct by replacing "$\epsilon = \frac{1}{100}$" by "$\epsilon = \frac{1}{200}$". When this change is made the argument reads correctly.

ZEEMAN EFFECT OF HYPERFINE STRUCTURE IN INTERMEDIATE FIELDS

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The theory of the Zeeman effect of ordinary fine structure in intermediate and high fields, developed by Heisenberg and Jordan,[1] Darwin[2] and Mensing,[3] has been modified by Goudsmit and Bacher[4] to suit the case of hyperfine structure and its Zeeman effect. This theory has been verified in the cases of Thallium II and III and Bismuth II and III by Green and Wulff[5] at field strengths of 14700, 32500 and 43350 gauss, using a large grating as the resolving instrument. The complete Paschen-Back effect for Hg^{199} has also been observed by Green.[6] Jackson and Kuhn[7] have observed an incomplete Paschen-Back effect in the case of potassium at 730 gauss, the results being in good agreement with theory. In the present work, the Zeeman effect of the hyperfine structure of the mercury green line Hg I λ 5461 Å has been studied at field strengths up to 4000 gauss. On account of the complicated structure of the line, attention has been mostly focussed on one particular satellite $+0{\cdot}753$ cm.$^{-1}$, which arises from the transition $7^3S_1\ f=\frac{3}{2} \rightarrow 6^3P_2\ f=\frac{3}{2}$ in the odd isotope Hg^{199} with a nuclear spin of $\frac{1}{2}$.[8] The results show a good agreement with theory both as regards separations as well as intensities. Thus while the complete Paschen-Back effect is the best spectroscopic evidence for the correctness of an assignment of nuclear spin, the Zeeman effect of hyperfine structure at lower fields can also provide substantial support to the value of the spin otherwise deduced.

Theoretical

The calculation of the expected Zeeman effect is based on the following theory. The positions of the levels in the magnetic field are found by writing down the equations :*

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[1] Heisenberg and Jordan, *Zeits. f. Physik*, 1926, **37**, 263.

[2] Darwin, *Proc. Roy. Soc.*, 1927, **115**, 1.

[3] Mensing, *Zeits. f. Physik*, 1926, **39**, 24.

[4] Goudsmit and Bacher, *Zeits. f. Physik*, 1930, **66**, 16.

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[6] ———, *Ibid.*, 1936, **50**, 126.

[7] Jackson and Kuhn, *Proc. Roy. Soc.*, 1938, **165**, 303.

[8] Schüler and Jones, *Zeits. f. Physik*, 1932, **74**, 640.

* There is a misprint in connection with this formula in the original paper of Goudsmit and Bacher.

$$- X_{M_I+1, M_J-1} \frac{A}{2} (I + M_I + 1)(J - M_J + 1)$$

$$+ X_{M_I M_J} [E - A M_I M_J - M_J g(J) OH]$$

$$- X_{M_I-1, M_J+1} \frac{A}{2} (I - M_I + 1)(J + M_J + 1) = 0, \qquad (I)$$

[there being as many equations as there are values of M_I and M_J corresponding to a given $M_F = M_I + M_J$] and equating their determinant to zero and solving the resulting equation for E. Here E is the distance of the level from the centre of gravity of the hyperfine multiplet level. In the case of the satellite under consideration which belongs to Hg^{199}, $I = \frac{1}{2}$, so that $M_I = \pm \frac{1}{2}$, and we have only two equations of the type (I) and their determinant equated to zero yields a quadratic. The values so obtained for E are given below. g (J) has been calculated on the assumption that Russell-Saunders coupling exists. In these equations O is the Larmor frequency. Expressing E and O in cm.$^{-1}$, $O = 4{\cdot}67 \times 10^{-5}$ cm.$^{-1}$.

6^3P_2: $M_F = \frac{3}{2}$; $2E = -\frac{A}{2} + \frac{3}{2} OH - \sqrt{6\frac{1}{4} A^2 - \frac{3}{2} AOH + \frac{9}{4} O^2H^2}$

$M_F = \frac{1}{2}$; $2E = -\frac{A}{2} + \frac{3}{2} OH - \sqrt{6\frac{1}{4} A^2 - \frac{3}{2} AOH + \frac{9}{4} O^2H^2}$

$M_F = -\frac{1}{2}$; $2E = -\frac{A}{2} - \frac{3}{2} OH - \sqrt{6\frac{1}{4} A^2 + \frac{3}{2} AOH + \frac{9}{4} O^2H^2}$

$M_F = -\frac{3}{2}$; $2E = -\frac{A}{2} - \frac{3}{2} OH - \sqrt{6\frac{1}{4} A^2 + \frac{3}{2} AOH + \frac{9}{4} O^2H^2}$

7^3S_1: $M_F = \frac{3}{2}$; $E = \frac{A}{2} + 2 OH$

$M_F = \frac{1}{2}$; $2E = -\frac{A}{2} + 2 OH + \sqrt{2\frac{1}{4} A^2 - 2AOH + 4 O^2H^2}$

$M_F = -\frac{1}{2}$; $2E = -\frac{A}{2} - 2 OH + \sqrt{2\frac{1}{4} A^2 + 2AOH + 4 O^2H^2}$

$M_F = -\frac{3}{2}$; $E = \frac{A}{2} - 2 OH.$

The values of E having been found, the expected Zeeman-pattern is computed, remembering that $\Delta M_F = 0$ for π-components and $\Delta M_F = \pm 1$ for σ-components. The component lines are here referred to the centre of gravity of the field-free hyperfine multiplet.

The values of E thus obtained being substituted in (I), we can solve them for the X's when the normalizing condition

$$\sum_{M_F = \text{const.}} X^2_{M_I M_J} (I + M_I)!\,(I - M_I)!\,(J + M_J)!\,(J - M_J)! = 1 \qquad (II)$$

is added. When the X's have been thus found, the intensities of the Zeeman components are calculated according to the following formulæ :

Transition $J \rightarrow J'$ $(J' = J - 1)$

π-Components :

$M'_F = M_F$ $\quad$ Int. $= 4 \left[\sum_{M_F \text{ const.}} X_\mu X'_\mu \, (I+M_I)\,!\,(I-M_I)\,!\,(J+\mu)\,!\,(J-\mu)\,!\right]^2$

σ-Components :

$M'_F = M_{F-1}$ $\quad$ Int. $= \left(\Sigma X_\mu X'_{\mu-1} \, (I+M_I)\,!\,(I-M_I)\,!\,(J+\mu)\,!\,(J-\mu)\,!\right]^2$

$M'_F = M_{F+1}$ $\quad$ Int. $= \left(\Sigma X_\mu X'_{\mu+1} \, (I+M_I)\,!\,(I-M_I)\,!\,(J+\mu)\,!\,(J-\mu)\,!\right]^2$,

where $\mu = M_J$ such that M_F is constant.

Transition $J \rightarrow J'$ $(J' = J)$

π-Components

$M'_F = M_F$ $\quad$ Int. $= 4 \left[\Sigma X_\mu X'_\mu (I + M_I)\,!\,(I - M_I)\,!\,(J + \mu)\,!\,(J - \mu)\,!\right]^2$

σ-Components :

$M'_F = M_F - 1$ $\quad$ Int. $= \left[\Sigma X_\mu X'_{\mu-1} \, (1+M_I)\,!\,(I-M_I)\,!\,(J+\mu)\,!(J-\mu+1)\,!\right]^2$

$M'_F = M_F + 1$ $\quad$ Int. $= \left[\Sigma X_\mu X'_{\mu+1} \, (I + M_I)\,!\,(I - M_I)\,!\,(J + \mu + 1)\,!\,(J - \mu)\,!\right]^2$

'A' for the 6^3P_2 level is $303{\cdot}2 \times 10^{-3}$ cm.$^{-1}$ and that for the 7^3S_1 level is $713{\cdot}3 \times 10^{-3}$cm.$^{-1}$. With these values the separations of the various Zeeman components of the satellite $+ 0{\cdot}753$ cm.$^{-1}$ from its field-free position, as also their intensities, have been calculated and the results are given in the tables below ; the intensities are given within brackets.

TABLE I

π-components $(+ 0{\cdot}753$ cm.$^{-1})$

H in gauss	$10^3 \times \Delta\nu$ in cm.$^{-1}$ (Intensity) A	B*	C*	D	I_A/I_D
2000	− 60·8 (3·23)	− 7·9 (0·30)	+ 34·5 (0·22)	+ 69·1 (1·80)	1·9
2500	− 74·3 (3·49)	− 5·2 (0·31)	+ 46·8 (0·21)	+ 87·4 (1·68)	2·1
3000	− 87·1 (3·76)	− 0·7 (0·31)	+ 60·5 (0·19)	+106·0 (1·56)	2·4
3500	− 99·9 (4·05)	+ 5·7 (0·31)	+ 75·4 (0·18)	+128·9 (1·46)	2·8
4000	−110·2 (4·34)	+13·9 (0·31)	+ 91·4 (0·17)	+144·1 (1·37)	3·2

* Not observed because of their relatively small intensity.

TABLE II

σ-components ($+ 0.753$ cm.$^{-1}$)

H in gauss	$\Delta\nu \times 10^3$ cm.$^{-1}$ (Intensity) a*	b*	c*	d	e	f	$\frac{\Delta\nu_{de}}{\Delta\nu_{ef}}$
2000	− 177·8 (0·88)	− 133·2 (0·97)	− 96·8 (0·63)	+ 109·1 (0·98)	+ 159·8 (1·06)	+ 200·4 (0·67)	1·25
2500	− 218·0 (0·89)	− 162·4 (0·95)	− 119·3 (0·59)	+ 138·5 (1·03)	+ 204·0 (1·05)	+ 253·5 (0·64)	1·33
3000	− 256·4 (0·89)	− 190·3 (0·91)	− 141·0 (0·56)	+ 168·6 (1·07)	+ 250·1 (1·02)	+ 307·5 (0·61)	1·42
3500	− 293·8 (0·88)	− 216·5 (0·87)	− 162·3 (0·53)	+ 199·6 (1·12)	+ 297·6 (1·00)	+ 362·6 (0·58)	1·50
4000	− 327·6 (0·88)	− 241·5 (0·83)	− 183·0 (0·49)	+ 231·3 (1·17)	+ 346·8 (0·97)	+ 418·5 (0·55)	1·61

* Not observed due to overlapping.

Tables III and IV give the computed Zeeman effect of the hyperfine structure component $-0{\cdot}315$ cm.$^{-1}$ of λ 5461 Å arising from the transition $7^3S_1\, f=\frac{1}{2} \rightarrow 6^3P_2\, f=\frac{3}{2}$ in the odd isotope Hg^{199} for the above intermediate field strengths.

TABLE III

π-components ($-0{\cdot}315$ cm.$^{-1}$)

H	$\Delta\nu \times 10^3$ cm.$^{-1}$ (Intensity)	
2000	− 41·4 (13·05)	+ 39·2 (13·67)
2500	− 52·0 (12·99)	+ 48·6 (13·75)
3000	− 62·5 (12·94)	+ 57·6 (13·86)
3500	− 73·2 (12·88)	+ 66·5 (13·94)
4000	− 83·9 (12·83)	+ 75·0 (14·03)

TABLE IV

σ-components ($-0{\cdot}315$ cm.$^{-1}$)

H	$\Delta\nu \times 10^3$ cm.$^{-1}$ (Intensity)			
2000	− 209·1 (3·05)	− 130·7 (9·50)	+ 124·5 (10·42)	+ 206·9 (3·67)
2500	− 261·2 (2·99)	− 164·2 (9·36)	+ 154·7 (10·52)	+ 257·8 (3·76)
3000	− 313·3 (2·93)	− 198·1 (9·23)	+ 184·5 (10·59)	+ 308·4 (3·86)
3500	− 365·1 (2·88)	− 233·0 (9·08)	+ 214·0 (10·68)	+ 358·4 (3·94)
4000	− 416·8 (2·83)	− 266·5 (8·93)	+ 243·2 (10·76)	+ 407·9 (4·03)

Experimental

The low density mercury vacuum arc lamp employed in this investigation was of a special type. A primary arc carrying a current of 4 amps. was maintained between the water-cooled cathode K (Fig. 1) and the tungsten anode A 1. A low current ($< \frac{1}{2}$ amp.) secondary arc was next started between K and the anode A 2; the vertical long tube (nearly 20 cms. long) with the low current arc was placed between the parallel pole-pieces of an electromagnet. The diameter of the flat pole-pieces was about 4 cms.; about 2 cms. of the arc-length in the centre of the magnetic field was considered to lie in a uniform field and was therefore isolated for study by properly screening the rest of the arc. The local heating of the Pyrex glass

tube produced by the deflection of the arc in the magnetic field was small, because of the low current in the arc. The light of the arc in the field was passed through a nicol and then condensed on to an adjusted Fabry-Perot etalon of the Lesche type in front of which was placed a green-ray filter.

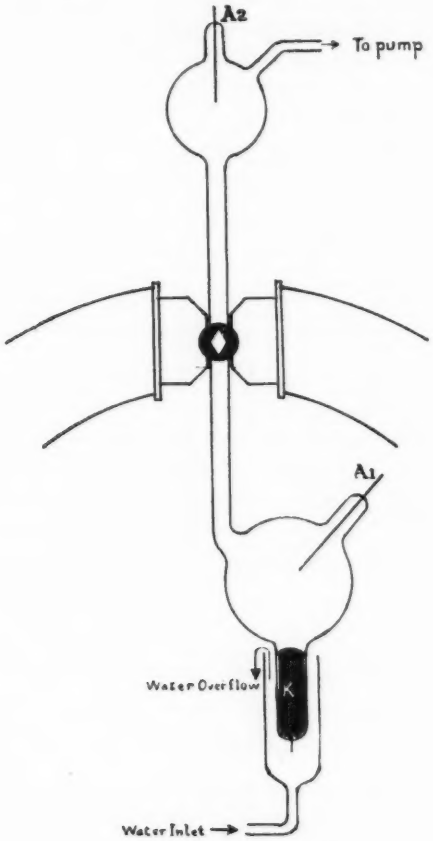

FIG. 1 Source

The invar distance pieces (2·5 mms. and 3 mms. thick) were selected so as to bring the satellite $+0{\cdot}753$ cm.$^{-1}$ of the mercury line Hg I λ 5461 Å into the middle of the pattern; in the immediate vicinity of this satellite there was no other component which could have vitiated our results. The Zeeman effect of the satellite was in several cases directly measured by means of a micrometer eyepiece in the observing telescope placed immediately after

the Fabry-Perot etalon. But the comparison of the relative intensities of the components necessitated the photographing of the pattern, and this was done by a camera substituted in place of the telescope. Hypersensitive Panchromatic plates were used and a special fine grain developer was employed. Fig. 2 is a reproduction of a typical pattern showing the Zeeman π-components of the satellite $+0{\cdot}753$ cm.$^{-1}$ in the magnetic field. The intensity curves in Fig. 3 were obtained on a Moll Recording Microphotometer by the kind permission of Sir C. V. Raman at the Indian Institute of Science. The magnetising current was carefully controlled and maintained constant during measurement and photography. The field strength was measured directly by a flux-meter and a check on this value was obtained by estimating the field strength from the Zeeman splitting of the main line; these two independent methods gave values agreeing within 2 per cent. The results of visual measurements were consistent with theoretical expectations; the values obtained from a few of the photographed patterns whose intensity curves have been reproduced in Fig. 3, are given in Table V and compared with the results of theoretical calculation. In the case of the σ-components, only one half of them *d*, *e*, *f* could be observed as the other half *a*, *b*, *c* got merged with the main components. The ratio of the intensities of the π-components A and D, and the separation between them were plotted against the field strength H, to get their values at the particular field strengths employed; these calculated values were then compared with the observed values. Similarly in the σ-components, the ratio $\Delta\nu_{de}/\Delta\nu_{ef}$ has been obtained by the same method for any particular field.

TABLE V

	Fig. 3	H in gauss	$\Delta\nu_{AD}$ in cm.$^{-1}$		I_A/I_D	
			Calc.	Obs.	Calc.	Obs.
π-components				$\pm$ 0·005		$\pm$ 0·3
	1	2127	0·134	0·137	1·95	2·0
	2	2596	0·168	0·164	2·14	2·2
	3	4032	0·256	0·256	3·23	3·0
σ-comp.			Calc		Obs.	
	4	3700	$\frac{\Delta\nu_{de}}{\Delta\nu_{ef}} = 1{\cdot}56$		$\frac{\Delta\nu_{de}}{\Delta\nu_{ef}} = 1{\cdot}5$	

Table V shows a satisfactory agreement between the calculated and observed values in the separations as well as the relative intensities of the Zeeman components of the satellite $+0{\cdot}753$ cm.$^{-1}$. The separations of the components for field-strengths below 4000 gauss nearly coincide with the values computed on the basis of the weak field theory which gives $\pm \frac{(7),\ (21),\ 33,\ 47,\ 61}{30}$ OH with relative intensities (1) : (9) : 3 : 4 : 3 respectively ; and small deviations have been observed only above 4000 gauss. But the relative intensities of the π-components A and D, which should be equal according to the weak field theory, show agreement only with the results of the theory for intermediate fields. Because of the proximity of the other satellites the Zeeman effect study of $-0{\cdot}315$ cm.$^{-1}$ was carried out at field strengths below 2500 gauss, and no deviation either in separation or in intensity from the values given by the weak field theory was observable. The computed results set forth in Tables III and IV for intermediate fields show little deviation at these field strengths from the weak field theory, which gives $\pm \frac{(13),\ 41,\ 67}{30}$ OH for the separations with relative intensities (4) : 3 : 1 respectively. With the field strengths employed, the intensities of the Zeeman components of $-0{\cdot}315$ cm.$^{-1}$ computed for intermediate fields show no observable deviation from the results for weak fields.

In conclusion we thank Prof. B. Venkatesachar for initiating this work and giving us helpful suggestions. We are also indebted to Prof A. Venkat Rao Telang for his kind encouragement.

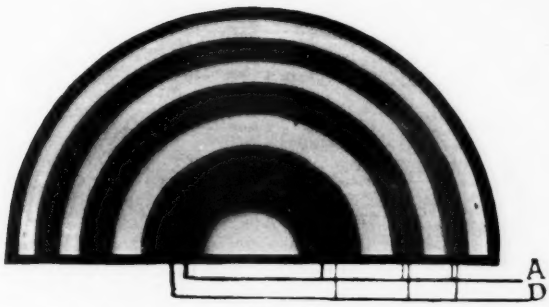

FIG. 2

π- components (A & D) of $+ 0{\cdot}753$ cm.$^{-1}$ showing their relative intensities in a magnetic field H = 4032 gauss

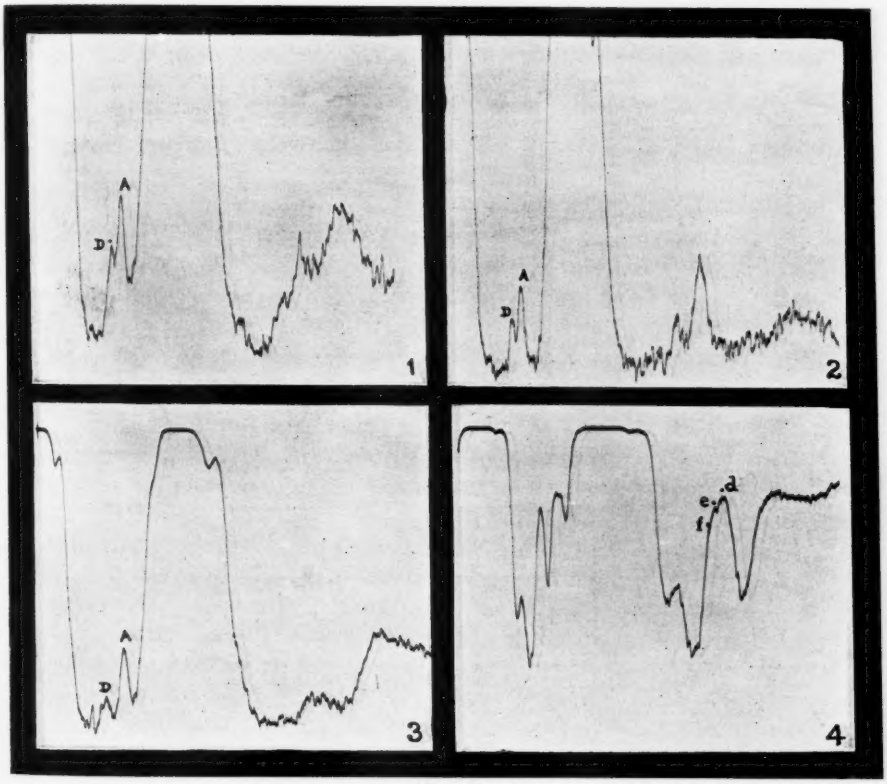

FIG. 3

Microphotographs of π- and σ-components

ON THE SELF-REVERSAL OF SPECTRAL LINES

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Introductory

The arc spectra of elements sometimes yield lines in which the cores have been absorbed and are replaced by dark lines; this phenomenon, which is common especially in the resonance lines of elements, has been here referred to as the self-reversal of spectral lines. Hyperfine structure study of spectral lines has often been vitiated by this phenomenon, which doubles the main lines and sometimes the satellites also, thereby giving a false pattern for the structure of the lines. Sources giving rise to self-reversal have therefore been carefully avoided in all recent work on hyperfine structure. Apart from an anxiety to avoid sources that introduce complications arising out of self-reversal, I am not aware of any attempt to study the peculiarities of the self-reversed spectral lines. In my study of the hyperfine structure of the arc lines of various elements, such as copper[1], molybdenum,[1] gold,[2] silver,[3] etc., the self-reversed spectral lines have been encountered. Measurements on the reversed lines obtained from cooled hollow cathode sources have led me to infer that the extent of self-reversal in the various lines of a given multiplet is not the same; for instance under the same conditions of discharge the two silver lines $^2S_{\frac{1}{2}} - {}^2P_{\frac{1}{2},\frac{3}{2}}$ exhibit different amounts of self-reversal; but the ratio of the reversal separations in the two lines remains constant under all conditions of excitation. The same result has been obtained with the resonance lines of copper. Thus in such line pairs as these, though the individual reversal separations are different and depend on various factors, it is observed that the ratio of the reversal separations in the lines is constant and independent of the physical conditions in the source. There is yet another interesting feature. When each of the gross-multiplet lines is considered for simplicity to consist only of two hyperfine structure components as it is in the resonance lines of copper and gold, the self-reversals in the two components of the same arc lines are observed to be unequal. Here also it

[1] Sibaiya, *Proc. Ind. Acad. Sci.*, 1934, **1**, 321.
[2] —, *Ibid.*, 1935, **2**, 313.
[3] Not published.

has been found that the reversal ratio between the main line and the satellite is a constant independent of the conditions in the source. An explanation of these observations on the basis of the classical dispersion theory is attempted below ; it is followed by a brief discussion of the experimental data in the light of the theoretical conclusions.

Theoretical

Neglecting quantities of the second order, Minkowski[4] and Korff[5] have shown that the classical dispersion theory of Lorentz[6] and Voigt[7] gives for the distribution of energy within a spectral line arising from absorption by a finite thickness of absorbing vapour at moderate temperatures an expression, which according to Korff, is

$$(\Delta\lambda)^2 \log \epsilon \frac{I}{I_0} = -\frac{2\pi e^4 \lambda^2{}_0}{3m^2c^4} N \qquad \text{(i)}$$

where I_0 is the intensity of the continuous background,

e, m, charge and mass of the electron respectively,

λ_0, the wavelength of the line under consideration,

$\Delta\lambda$, the wave-length separation of given line from the resonance line λ_0,

I, the intensity of the transmitted light at the given wavelength $\lambda_0 \pm \Delta\lambda$,

c, the velocity of light, and

N, the number of absorbing centres (linear oscillators) per sq. cm. in the line of of sight.

The method of computing N is important. If we should take any element of the alkali group as an example, the number of absorbing centres corresponding to each member of the doublet is taken as $N = n\,z\,f$ where n is the number of absorbing atoms per c.c., z the length of the absorbing column, and f the oscillator strength or the proportion of atoms being raised by absorption to the particular doublet state involved. A consideration of the statistical weights of the doublet states $^2P_{\frac{1}{2}}$, $^2P_{\frac{3}{2}}$ gives for f the values $\frac{1}{3}$ and $\frac{2}{3}$; *i.e.*, the ratio of the f values of the two states is equal to the ratio of the quantum weights $(2j + 1)$ of the levels.

In the case of a source, the radiation from which is showing self-reversal, the background intensity for absorption is not a constant ; it is given by the

[4] Minkowski, *Z.P.*, 1936, **36**, 839.
[5] Korff, *A.J.*, 1932, **76**, 124.
[6] Lorentz., *Proc. Amst. Acad.*, 1905, **8**, 591.
[7] Voigt, *Münich Ber.*, 1912, p. 603.

radiated line, which by Doppler broadening has, according to Rayleigh,[8] the intensity distribution:

$$I_0 = J\ \epsilon^{-\frac{M}{2R\theta}\frac{c^2}{\lambda^2_0}(\Delta\lambda)^2},$$

where

J is the intensity at the core λ_0,
M, the mass of the radiating centre,
R, Boltzmann constant per atom, and
θ, the absolute temperature.

Assuming that a radiation with the above intensity distribution is subsequently absorbed by the absorbing column, the resulting intensity distribution in the self-reversed line is given by

$$I = J\ \epsilon^{-\frac{Mc^2}{2R\theta}\frac{(\Delta\lambda)^2}{\lambda^2_0}}\ \epsilon^{-\frac{2\pi e^4 N}{3m^2c^4}\frac{\lambda^2_0}{(\Delta\lambda)^2}}.$$

The intensity after absorption, I, will therefore be zero, when $\Delta\lambda = 0$ and again when $\Delta\lambda \rightarrow \pm\infty$, *i.e.*, when $\lambda = \lambda_0$ and $\lambda = \pm\infty$ respectively. The wave-length distance of the intensity maximum from λ_0 should now be calculated. Writing $(\lambda_0 - \lambda)$ for $(\Delta\lambda)$, we get

$$\log \epsilon \frac{I}{J} = -\frac{Mc^2}{2R\theta}\left(1 - \frac{\lambda}{\lambda_0}\right)^2 - \frac{2\pi e^4 N}{3m^2c^4}\left(1 - \frac{\lambda}{\lambda_0}\right)^{-2}.$$

Differentiating,

$$\frac{dI}{d\lambda} = \frac{I}{\lambda_0}\left[\frac{Mc^2}{R\theta}\left(1 - \frac{\lambda}{\lambda_0}\right) - \frac{4\pi e^4 N}{3m^2c^4}\left(1 - \frac{\lambda}{\lambda_0}\right)^{-3}\right].$$

If $\Delta\lambda = \lambda_0 - \lambda$ in the above equation, corresponds to the reversal maximum, then $\frac{dI}{d\lambda} = 0$ whence

$$\Delta\lambda = \lambda_0\left(\frac{4\pi e^4 R\theta}{3M m^2 c^6}\right)^{\frac{1}{4}} N^{\frac{1}{4}}.$$

The wave-number separation $\Delta\nu$ between the two maxima produced by self-reversal is given by

$$\Delta\nu = \left(\frac{64\pi e^4 R\theta}{3M m^2 c^6}\right)^{\frac{1}{4}} \frac{N^{\frac{1}{4}}}{\lambda_0}$$

$$= \left(\frac{64\pi e^4 R}{3m^2 c^6}\right)^{\frac{1}{4}} \left(\frac{\theta n z}{M}\right)^{\frac{1}{4}} \frac{f^{\frac{1}{4}}}{\lambda_0}$$

$$= 0{\cdot}95 \times 10^{-15} \left(\frac{\theta n z}{M}\right)^{\frac{1}{4}} \frac{f^{\frac{1}{4}}}{\lambda_0}. \qquad \text{(ii)}$$

Thus the reversal separations in wave-numbers in any multiplet group are, under given conditions of excitation which determine the values of θ,

[8] Rayleigh, *Phil. Mag.*, 1915, **29**, 274–284.

n and z, proportional to $f^{\frac{1}{4}}/\lambda_0$. When we compare the reversals in the two lines λ_1 and λ_2 of the doublet ${}^2S_{\frac{1}{2}} - {}^2P_{\frac{1}{2},\frac{3}{2}}$ where the statistical weights f_1 and f_2 of the upper levels are $\frac{1}{3}$ and $\frac{2}{3}$ respectively, we obtain

$$\frac{\Delta\nu_2}{\Delta\nu_1} = \frac{f_2^{\frac{1}{4}}}{\lambda_2} \Big/ \frac{f_1^{\frac{1}{4}}}{\lambda_1} = 2^{\frac{1}{4}} \frac{\lambda_1}{\lambda_2}. \qquad \text{(iii)}$$

Generally, however, $\frac{f_2}{f_1} = \frac{2j_2+1}{2j_1+1}$, the j-values being those of the levels not common to the two lines.

When two hyperfine components having a common upper or lower hyperfine level are reversed, because $\lambda_1 \gtrless \lambda_2$ we have

$$\frac{\Delta\nu_2}{\Delta\nu_1} = \left(\frac{f_2}{f_1}\right)^{\frac{1}{4}} = \left(\frac{2\mathbf{f}_2+1}{2\mathbf{f}_1+1}\right)^{\frac{1}{4}} \qquad \text{(iv)}$$

where the **f** values are the hyperfine quantum numbers of the levels not common to the two components. Since the intensity of a component is proportional to the quantum weight, it follows that the reversal is directly proportional to the fourth root of the intensity.

Comparison with Experimental Results

In support of the theoretical conclusions, a few results of experimental observation will next be given. These results were obtained in the course of the hyperfine structure study of the spectral lines of elements radiated from water-cooled hollow cathode sources carrying 100-200 ma. at about 1000 V in an atmosphere of helium at 2 mms. pressure. It may be pointed out that the assumptions both implied and expressed in deducing the above relations are to a great extent satisfied only in such sources as these and not in open electric arcs. Quartz Lummer-Gehrcke plates were employed in determining the extent of self-reversal, which at no time exceeded $0{\cdot}3$ cm.$^{-1}$ under the conditions of the experiment. In the case of silver, using (iii),

$$\frac{(\Delta\nu)_{2P_{\frac{3}{2}}-2S_{\frac{1}{2}}}}{(\Delta\nu)_{2P_{\frac{1}{2}}-2S_{\frac{1}{2}}}} = (2)^{\frac{1}{4}} \frac{3383}{3280} = 1{\cdot}23,$$

the mean observed value under two different conditions of discharge is $1{\cdot}21$.

Again in the case of copper,

$$\frac{(\Delta\nu)_{2P_{\frac{3}{2}}-2S_{\frac{1}{2}}}}{(\Delta\nu)_{2P_{\frac{1}{2}}-2S_{\frac{1}{2}}}} = (2^{\frac{1}{4}}) \frac{3274}{3247} = 1{\cdot}20,$$

as against the observed value $1{\cdot}22$.

Considering the case of the hyperfine structure we have in the two components of each of the ${}^2S_{\frac{1}{2}} - {}^2P_{\frac{1}{2},\frac{3}{2}}$ copper lines, where in consequence of the

nuclear spin moment $\frac{3}{2}$, the two **f** values in $^2S_{\frac{1}{2}}$ level are 1 and 2, using (iv),

$$\frac{(\Delta\nu)_{\text{main}}}{(\Delta\nu)_{\text{satellite}}} = \left(\frac{5}{3}\right)^{\frac{1}{4}} = 1{\cdot}14,$$

while the observed value is 1·15. The agreement between the observed and the calculated values should be considered good, on account of the difficulty in the accurate determination of reversal separations in practice. The absorption formula (i) has been subjected by Heard,[9] to experimental test by examining the contours of the resonance lines of potassium λ 7665 and λ 7699 in absorption by a method of photographic photometry. His results are in accordance with the classical dispersion theory of line width for a number of atoms per c.c. less than $0{\cdot}80 \times 10^{14}$; but even in this region the observed and calculated values show often a deviation of about 10%. A direct verification of (i) is beset with many difficulties; important among them are the accurate determination of the intensities at various points of the absorption line and the correct estimate of N which contains two uncertain factors n and z, the latter being capable of more accurate determination. These difficulties do not arsie in the comparison of reversal separations and a greater measure of agreement is noticed in accord with expectations.

Apart from this agreement between the theoretical and the observed ratio of the self-reversal separations, the absolute value of the reversal separation was computed for copper and silver lines by assuming probable values for θ, n and z, and using the relation (ii). The calculated and the observed values were of the same order. In long column sources where the emitting and absorbing centres coexist, Venkatesachar[10] has shown that the lines are broadened with the intensity distribution given by

$$I_0 = J\,\frac{1 - \epsilon^{-A_0 Z \epsilon^{-k(\Delta\lambda)^2}}}{1 - \epsilon^{-A_0 Z}}$$

where A_0 is the absorption coefficient at λ_0 and $k = \dfrac{M}{2R\theta}\,\dfrac{c^2}{\lambda^2_0}$. When $\Delta\lambda = 0$ the intensity at the centre λ_0 becomes $I_0 = J$ thus exhibiting no reversal. It is therefore necessary for self-reversal to consider the emitted lines as passing through the absorbers placed separately after the emitters. In metallic arcs, for instance, the radiation from the luminous core is reversed while passing through the outer envelope of comparatively cooler vapour surrounding the core.

In conclusion, I wish to thank Professor A. Venkat Rao Telang for his valuable guidance.

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[9] Heard, *Month. Not. Roy. Astro. Soc.*, 1934, **94**, 458–466.

[10] Venkatesachar, *Phil. Mag.*, 1925, **49**, 33–59.

RAMAN EFFECT IN RELATION TO CRYSTAL STRUCTURE

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I. Introduction

It is now widely recognised that a study of the Raman effect furnishes a convenient and powerful method of solving several problems of physical and chemical interest. During the past ten years, its applications have been varied and numerous as may be seen from the very large number of original communications that have appeared from time to time. Amongst the major fields of investigation thus opened up, mention may be made of the structure of molecules, nature of interatomic forces, electrolytic dissociation, formation of molecule complexes, etc. Numerous as have been its successes in the above fields, there is little doubt that this discovery is capable of yielding much more and that it has not yet been made use of to the fullest extent to which it is possible. In this connection it is of interest to recall the following remarks of Lord Rutherford.[1] 'The Raman

[1] *Proc. Roy. Soc.*, 1931, (A), **130**, 259.

effect must rank among the best three or four discoveries in experimental physics of the last decade. It has proved, and will prove, an instrument of *great power in the study of the theory of solids.*" This latter aspect is of special importance in connection with the physics of the solid state but has not yet been the subject of any intensive investigation. The comparative ease with which experimental data may be collected in liquids has resulted in the accumulation of a wealth of information relating to this branch but the advance has not been so marked in the case of solids. The experimental difficulties arising out of the fact that it is not easy to get large and transparent solid lumps have been the chief obstacles in the latter case. Special methods have nevertheless been devised and some progress has been made even with crystals.

No systematic attempt has however so far been made to correlate the meagre results that are available with the known crystalline properties. Results of great complexity are usually obtained with crystals and their interpretation has hitherto been merely empirical. A proper study of the normal modes of oscillation of a crystal with special reference to the selection rules in Raman effect and infra-red absorption is likely to throw considerable light on a variety of detail such as the appearance of several additional component lines in crystals, the origin of low frequency Raman bands in certain solids, the relationship of such bands to the wings in the corresponding liquids, the variations which the Raman spectrum undergoes as we pass from one crystalline modification to another, the dependence of the characteristics of Raman lines on the direction and manner of excitation and many other similar problems.

Apart from throwing light on such details, these studies may confidently be expected to bring into evidence the connection between Raman effect and certain other physical properties of crystals. The Raman spectrum results may be broadly divided into three branches, namely, those relating to (i) the fine structure of the Rayleigh lines, (ii) Raman lines due to the oscillations of the lattice groups as a whole and (iii) Raman lines due to internal oscillations of the atoms within the groups themselves. Results in respect of the first item are closely connected with the elastic properties of the crystal. On the other hand, the symmetry of the crystal and the disposition of the atoms and molecules in the lattice will determine the appearance or otherwise of Raman lines corresponding to specific normal modes coming under the second and the third items. It may be mentioned here that when a group of ions or molecules, each of which is characterised by a certain degree of symmetry are built into a crystal lattice having a lower degree of symmetry, some of the degenerate normal modes may be expected to split up. Thus the results

in respect of the lattice and the internal oscillations are very intimately connected with crystal structure. Next in importance is the subject of specific heat of solids. A complete analysis of the normal modes of oscillation of a crystal and a verification of the same with the help of Raman and infra-red absorption spectra is obviously of great help in evaluating its specific heat. Among the other fields which have a bearing on this branch of investigation, mention may be made of the anisotropic properties of crystals in respect of refraction, magnetic susceptibility, thermal expansion, etc. The effect of temperature on the positions and sharpness of Raman lines, particularly those coming under the category of lattice oscillations, is of special interest as it is likely to throw light on the nature of the crystalline forces and how they are released with increasing temperature. The gradual transition of these bands into the continuous wing usually encountered with in the molten state is intimately connected with the mechanism of melting. Thus practically all the important physical properties of a crystal are brought into the discussion when we attempt to explain the phenomenon of light scattering in crystals.

Brester,[2] Dennison[3] and others have studied the normal modes of some symmetrical systems by employing certain special methods. Wigner[4] has recently shown that the application of group theory to a study of the molecular oscillations greatly facilitates the work. Other investigators such as Tisza,[5] Wilson,[6] Placzek[7] and Rosenthal and Murphy[8] have subsequently made important contributions to the subject. In the present investigation, an account of this theory is given in a form that is applicable to crystals. The question of selection rules has been examined in detail and a section dealing with the same is included. The methods have been applied to a few simple cases of crystals and the results are discussed with special reference to Raman effect with a view to illustrate the more important points.[9]

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[2] *Kristallsymetrie und Reststrahlen. Diss. Utrecht*, 1923 ; *Z. f. Phys.*, 1924, **24**, 324.
[3] *Rev. Mod. Phys.*, 1931, **3**, 280.
[4] *Göttinger Nachrichten*, 1930, 133.
[5] *Z. f. Phys.*, 1933, **82**, 48.
[6] *Phys. Rev.*, 1934, **45**, 706.
[7] *Handbuch Der Radiologie*, 1934, **2**, 205.
[8] *Rev. Mod. Phys.*, 1936, **8**, 317.
[9] A comprehensive account of the theory formally applicable to crystals is purposely included with a view to make the paper self-contained. A similar treatment in a form that is applicable to molecules has already been published by Tisza and by Rosenthal and Murphy. Attempts have been made to draw physical analogies wherever possible. The more important conclusions are given in italics and a reader who is interested only in the application of the group theoretical methods will find these statements useful.

II. Groups and Group Characters

Rosenthal and Murphy have given an excellent exposition of the subject in the paper already referred to and a detailed description need not be attempted here. Some of the theorems which have to be used in the following sections may be enunciated.

All the symmetry operations of a crystal lattice furnish a typical illustration of the elements of a group. If G is any abstract group and H is a group of linear substitutions and if to every element A of G there corresponds an element A′ of H such that the product of two elements A and B of G corresponds to the product of the two corresponding elements A′, B′ of H, then the group of matrices H is called a representation of G.

The character of a group element is the same in equivalent representations.

A group of homogeneous linear substitutions is spoken of as *reducible*, if it is possible to find a set of linear functions of the variables $(X_1, X_2, .., X_n)$ less in number than the variables such that they are transformed among themselves by every operation of the group. If it is not possible to find such a set of linear functions of the variables, the group of substitutions is said to be *irreducible*. A reducible group of homogeneous linear substitutions is called completely reducible when it is possible to choose the variables in such a way that (i) they fall into sets, each set of variables being transformed among themselves by every operation of the group while (ii) the group in each set is irreducible.

III. Normal Modes of Oscillation of a Crystal Lattice

1. *Normal Modes and Irreducible Representations.*—We will now regard all the equivalent points of the lattice as having the same motion at a given instant of time. Accordingly, we need describe the position of only one set of non-equivalent points for completely specifying the motion of the whole lattice. Let there be n non-equivalent points in a crystal lattice. The position of the atoms may be described by giving the $3n$ cartesian co-ordinates $x_1, y_1, z_1, .., x_n, y_n, z_n$ and they may be taken to correspond to zero values for the equilibrium position. For oscillations of small amplitudes, the potential and kinetic energies may be expressed as general quadratic functions of the co-ordinates. These may be simultaneously reduced to the canonical form

$$2\,V = \Sigma\,\lambda_i\,Q_i^2\,; \quad 2T = \Sigma\,\dot{Q}_i^2$$

with the help of suitable linear transformation of co-ordinates. $Q_1, Q_2, .., Q_{3n}$ are called the normal co-ordinates and the corresponding normal frequencies are given by the equations $4\pi^2\,\nu_k^2 = \lambda_k$. The normal co-ordinate gives the mode of oscillation. Thus, if

$$Q_k = \sum_l a_{kl}\,x_l + \sum_m b_{km}\,y_m + \sum_n c_{kn}\,z_n$$

is the expression for the normal co-ordinate Q_k in terms of the $3n$ cartesian co-ordinates of the n non-equivalent points, the amplitude of oscillation of the lth atom in the x direction is given by the coefficient of x_l, namely a_{kl}. The configuration of the lattice may now be denoted by Q_k. If we perform a symmetry operation R on the lattice, we get a new configuration which we denote by RQ_k. If by means of the operation R the kth atom goes over into the lth atom, we shall suppose that the lth atom remains in its own neighbourhood but gets the motion of the kth atom. By doing this for every atom we keep all the atoms in the neighbourhood of their original equilibrium positions and obtain a configuration of the lattice which is geometrically identical with RQ_k. If we denote this new configuration by RQ_k, $\overline{R}Q_k$ evidently represents a normal co-ordinate having the same frequency ν_k because the relative configuration of the atoms is not altered. If $\overline{R}Q_k$ is distinct from Q_k we obtain two distinct modes of oscillation having the same frequency ν_k. Such a case will not arise for non-degenerate modes of oscillation. Now if R runs through all the symmetry operations of the group G we get all the normal modes of oscillation belonging to the same frequency. But all these modes of oscillation may not be linearly independent.

Let $Q_1, Q_2, \ldots, Q_f$ be a set of linearly independent normal co-ordinates having the frequency ν_k. Then every other normal mode of oscillation with the frequency ν_k can be obtained as a superposition of these f normal modes of oscillations. The oscillation ν_k is therefore f-fold degenerate. Similarly we obtain the normal co-ordinates of different frequencies. Now the normal co-ordinates belonging to a definite frequency define an irreducible representation of the group G. For if $Q_1, Q_2, \ldots, Q_f$ are a set of normal co-ordinates with a certain frequency ν, the co-ordinates $Q_1, Q_2, \ldots, Q_f$ combine among themselves by the application of a symmetry operation and we cannot find linear combinations of $Q_1, Q_2, \ldots, Q_f$ smaller in number than f which combine among themselves by symmetry operations. Thus, if

$$\begin{aligned}
\overline{R}\,Q_1 &= a_{11}\,Q_1 \ldots\ldots\ldots + a_{1f}\,Q_f \\
\overline{R}\,Q_2 &= a_{21}\,Q_1 \ldots\ldots\ldots + a_{2f}\,Q_f \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
\overline{R}\,Q_f &= a_{f1}\,Q_1 \ldots\ldots\ldots + a_{ff}\,Q_f
\end{aligned}$$

then $R \rightarrow \overline{R} \rightarrow$ the matrix (a_{ij})

and the correspondence also defines a representation of the group G. *Thus a set of normal co-ordinates of a definite frequency define an irreducible representation.*

2. *Determination of the Number of Normal Modes that belong to a given Irreducible Representation.*—We divide the $3n$ normal co-ordinates into

different sets, each set belonging to a definite frequency. Let the irreducible representation defined by the rth set be denoted by $\mathrm{D}^{(r)}$. Then the reducible representation of all the normal co-ordinates may be denoted by

$$\mathrm{R} \rightarrow \Delta\,\mathrm{R} = \begin{vmatrix} \mathrm{D}^{(1)}(\mathrm{R}) & \cdot & \cdot & \cdot & \cdot \\ \cdot & \mathrm{D}^{(2)}(\mathrm{R}) & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

On the other hand, the $3n$ cartesian co-ordinates $x_1, y_1, z_1, \ldots, x_n, y_n, z_n$ define a reducible representation, for $\bar{\mathrm{R}}q$ where q stands for any one of $x_1, x_2, \ldots, z_n$ is a linear combination of them and therefore defines a representation of the group. It may easily be proved that this representation is equivalent to the above representation defined by the $3n$ normal co-ordinates and consequently the character of any group element R in the two representations is the same.

It is easy to calculate the character of any operation R from the reducible representation defined by the cartesian co-ordinates. If the symmetry operation R takes over the atom k into the atom l, we have in general $\mathrm{R}\,x_k = a_1 x_l + b_1 y_l + c_1 z_l$ and the character arising from x_k is 0. Similarly the character arising from y_k and z_k is 0. If on the other hand, the kth atom is invariant[10] under the operation R, we have

$$\begin{aligned} \bar{\mathrm{R}}\,x_k &= x_k \cos\phi + y_k \sin\phi \\ \bar{\mathrm{R}}\,y_k &= -x_k \sin\phi + y_k \cos\phi \\ \bar{\mathrm{R}}\,z_k &= z_k. \end{aligned}$$

In the above equations, the axis of rotation is taken as the z-axis itself and the x-and y-axes lie in a plane perpendicular to it. There is no loss of generality in the choice of such co-ordinates as the character is independent of the choice and we obtain $1 + 2\cos\phi$ for the character of an operation consisting of a rotation through ϕ radians. If the operation is a rotation reflection, we have the same relations as above except that $+z$ is replaced by $-z$ and the character comes out as $-1 + 2\cos\phi$. A simple reflection may be taken as a rotation through 0 radians accompanied by a reflection and a centre of inversion may be taken as a rotation through π followed by a reflection. We thus arrive at the result that an invariant atom under the operation R gives rise to the character $\pm 1 + 2\cos\phi_{\mathrm{R}}$ the $+$ or $-$ sign being used according as the operation is a pure rotation or a rotation reflection. The atoms which are not

[10] An atom should be considered invariant not only when it is in its own place but also when it occupies an equivalent position in the lattice as a result of the symmetry operation.

invariant do not contribute anything to the character of R. *Hence, in the reducible representation defined by the cartesian co-ordinates the character of any operation R is* ω_R $(\pm 1 + 2\cos\phi_R)$ *where* ω_R *is the number of invariant atoms under the operation R.* From a knowledge of the group characters in any representation Γ_i, we find n_i, the number of times a particular irreducible representation Γ_i is contained in Γ by means of the important formula[11]

$$n_i = \frac{1}{N} \sum_R \chi_i(R)\, \chi'(R), \qquad (1)$$

where χ_i (R) and χ'(R) are respectively the characters of R in Γ_i and Γ and N is the order of the group. In the above case where Γ stands for the reducible representation of the cartesian co-ordinates, χ'(R) is equal to ω_R $(\pm 1 + 2\cos\phi_R)$.

IV. Normal Co-ordinates

The first step in the application of the foregoing theory to an actual crystal consists in ascertaining its space group and writing down the appropriate character Table. The character Table in respect of each group is easily obtained from the general Tables already given by Tisza. We may then evaluate the character of each symmetry operation in the group for the reducible representation of the caretsian co-ordinates in the manner already explained. Since the character is the same for all operations coming under a particular class j we have

$$\sum_R \chi_i(R)\, \chi_i'(R) = \sum_j h_j \chi_i(R)\, \chi_i'(R)$$

The summation on the right-hand side extends over all the classes that constitute the group and h_j represents the number of elements in the jth class. Equation (1) of the foregoing section will now be rewritten as

$$n_i = \frac{1}{N} \sum_j h_j \chi_i(R)\, \chi_i'(R) \cdots \qquad (1\,a)$$

A knowledge of the number of atoms that remain invariant under each of the group operations R is necessary for evaluating n_i with the help of (1 *a*) and this number is also easily obtained. In the examples that have been analysed in the following sections of the present investigation, this number is denoted by ω_R and is included in the character Tables. The notation employed in respect of the other quantitites is the same as that used by Tisza. C^k and S^k in the case of a group possessing p-gonal symmetry stand for a pure rotation of $\frac{2\pi k}{p}$ and a rotation reflection of $\frac{2\pi k}{p}$ respectively. i and σ stand

[11] The actual value of n_i is obtained when χ_i (R) is replaced by its complex-conjugate but as we are dealing with real characters, this distinction is of no significance and has been ignored in the following sections of the paper.

for a centre of inversion and a plane of reflection respectively. χ_j' (R) is the character of an operation R coming under the class j in the reducible representation of cartesian co-ordinates.

In all the cases studied, the modes of oscillation are analysed with the help of the normal co-ordinates. x_i, y_i and z_i are the co-ordinates of the ith atom in a co-ordinate system whose origin is the equilibrium position of the atom in question. All these co-ordinate systems are parallel to each other and to a parent system which is suitably chosen. In order to obtain the normal co-ordinates corresponding to the non-degenerate oscillations, we start from the most general linear expression for Q in the $3n$ co-ordinates x_i, y_i, z_i. If R is an operation of the group, we have $RQ = \lambda Q$, where λ is the character corresponding to the operation R. We get one such relation corresponding to each operation of the group and these relations are sufficient to determine Q. For the determination of the normal co-ordinates of degeneracy r, we take r linear general expressions $Q_1, Q_2, \cdots, Q_r$ in the co-ordinates x_i, y_i, z_i. If R is an operation of the group, from relations like

$$RQ_k = \lambda_{1k} Q_1 + \lambda_{2k} Q_2, \cdots, \lambda_{rk} Q_r \; (k = 1, 2, \cdots, r)$$

we obtain the character of the operation R which is equal to $\Sigma\lambda_{kk}$. We again get as many relations as there are operations of the group. These relations along with the orthogonality conditions that should exist between the normal co-ordinates are in general sufficient to enable us to arrive at a set of normal co-ordinates. The normal co-ordinates should further satisfy the condition that the linear and angular momenta are conserved in every case except in those that correspond to pure translations and rotations. In giving the normal co-ordinates, the following conventions are adopted in the present paper. Q_x, Q_y, Q_z always represent the pure translations. The prefixes a and b attached to a normal co-ordinate indicate that they are degenerate with one another. Whenever a set of normal co-ordinates represented by dashes are connected by a parenthesis, it is to be understood that the actual modes of oscillation have to be obtained by forming independent combinations of the Q's themselves with coefficients which depend upon the force constants. The symbols T, L and i given immediately after the Q's in the normal co-ordinates denote that the corresponding modes refer respectively to pure translations, lattice and internal oscillations. In most of the cases except calcite, the normal co-ordinates are given in a very concise manner for the sake of brevity but by carefully studying the notation used, they may be written down explicitly with the least difficulty. The modes of oscillation are also represented diagrammatically in the case of calcite only and similar figures are omitted in other cases as they may be drawn in a like manner from the appropriate normal co-ordinates.

The knowledge obtained in the above manner at once enables us to classify the various normal modes as either pure translations or lattice oscillations or internal oscillations. This has been done for each irreducible representation in all the cases studied. Under the column ' external ', T and L respectively refer to pure translations and lattice oscillations. n_i' gives the number of internal oscillations under each irreducible representation. p and f in the last two columns respectively denote ' permitted ' and ' forbidden ' and refer to the activity or otherwise of the corresponding lines in Raman effect and infra-red absorption. These letters are appropriate only to the fundamental modes and the manner of obtaining them will be clear from the next section. Wherever necessary, an investigation is also made of the normal modes of oscillation of the free ions or groups of atoms that go to make up the crystals studied here with a view to correlate the Raman spectra obtained in the dissolved or molten states with those obtained in the corresponding crystals.

V. Selection Rules

1. *Fundamental Modes.*—It has been shown in the foregoing pages that every normal mode of oscillation belongs to an irreducible representation of the group of symmetry operations of the crystal. *The mode is active or inactive in the infra-red absorption according as it causes a variation or not in the electric moment of the molecule.* The variation itself may be regarded as a vector and Wigner has shown that this condition may be symbolically represented by

$$\sum_{R} (\pm 1 + 2\cos\phi_R)\,\chi_i(R) \begin{cases} = 0 \cdots \text{inactive} \\ \neq 0 \cdots \text{active} \end{cases} \qquad (2)$$

$\pm 1 + 2\cos\phi_R$ is the character of the operation R in the representation defined by the vector components and χ_i (R) is the character in the irreducible representation Γ_i to which the normal co-ordinate belongs. The summation extends over all the operations that constitute the group.

The selection rule for the Raman spectra may be derived in a like manner. *The mode is active or inactive according as it causes a variation or not in the optical polarisability of the molecule.* The variation itself may be regarded as a tensor and the condition which is symbolically represented by (3) is easily derived in the following manner.

Let $Q^{(1)}, Q^{(2)}, \cdots, Q^{(f)}$ be a complete set of f normal co-ordinates having the same frequency ν and let f_k be the vector displacement of the kth atom. We have

$$R\,Q^{(s)} = a_{1s}\,Q^{(1)} + a_{2s}\,Q^{(2)}, \cdots, a_{fs}\,Q^{(f)} = \sum_{\lambda=1}^{f} D(R)_{\lambda s}\,Q^{(\lambda)}.$$

Let $e_k\ f_k$ denote the change in the optical polarisability due to the displacement f_k of the kth atom. Then the ab component of the change in the optical polarisability due to the mode of oscillation represented by $Q^{(s)}$ is given by

$$\alpha_{ab}^{(s)} = \{e_1 f_1^{(s)}\}_{ab} + \{e_2 f_2^{(s)}\}_{ab} \cdots + \{e_n f_n^{(s)}\}_{ab}.$$

The following relation is now easily obtained :—

$$\overline{\mathrm{R}}\ \alpha_{ab}^{(s)} = \sum_{\lambda=1}^{f} \mathrm{D}\ (\mathrm{R})_{\lambda s} \{(e_1 f_1^{(\lambda)})_{ab} \cdots\cdots + (e_n f_n^{(\lambda)})_{ab}\}$$

$$= \sum_{\lambda=1}^{f} \mathrm{D}\ (\mathrm{R})_{\lambda s}\ \alpha_{ab}^{(\lambda)}.$$

On the other hand, α transforms itself as a tensor

$$\overline{\mathrm{R}}\ \alpha_{ab}^{(s)} = \sum_{i,j} \mathrm{R}_{a\,b\,i\,j}\ \alpha_{ij}^{(s)}.$$

Hence

$$\sum_{i,j} \mathrm{R}_{a\,b\,i\,j}\ \alpha_{ij}^{(s)} = \sum_{\lambda=1}^{f} \mathrm{D}\ (\mathrm{R})_{\lambda s} \alpha_{ab}^{(\lambda)}.$$

Therefore

$$\alpha_{ij}^{(s)} = \sum_{\lambda} \sum_{i,j} \mathrm{R}_{a\,b\,i\,j}\ \mathrm{D}\ (\mathrm{R})_{\lambda s}\ \alpha_{ab}^{(\lambda)}.$$

Summing the right-hand side for all group elements R, we find that it vanishes if the representation of G by the matrices $\mathrm{R}_{a\,b\,i\,j}$ is not contained in the irreducible representation D (R) defined by the normal co-ordinates corresponding to the frequency ν. The condition for this is that $\sum_{\mathrm{R}} \chi'\ (\mathrm{R})\ \chi_i\ (\mathrm{R}) = 0$. $\chi'\ (\mathrm{R})$ is the character of the operation R in the representation defined by the tensor components. $\chi'\ (\mathrm{R})$ is easily evaluated by choosing a convenient set of axes. Taking the axis of rotation as the z-axis itself, we obtain the following transformations for the tensor components with the help of the transformations given for the vector components in sub-section 2 of Section III for a similar case.

$$\overline{\mathrm{R}}\ \alpha_{xx} = \alpha_{xx} \cos^2\phi + \alpha_{yy} \sin^2\phi + \alpha_{xy} \sin\phi \cos\phi + \alpha_{yx} \sin\phi \cos\phi$$

$$\overline{\mathrm{R}}\ \alpha_{xy} = -\alpha_{xx} \sin\phi \cos\phi + \alpha_{xy} \cos^2\phi - \alpha_{yx} \sin^2\phi + \alpha_{yy} \sin\phi \cos\phi$$

$$\overline{\mathrm{R}}\ \alpha_{xz} = \alpha_{xz} \cos\phi + \alpha_{yz} \sin\phi$$

. . . . . .

$$\overline{\mathrm{R}}\ \alpha_{zz} = \alpha_{zz}$$

when R is a rotation through ϕ and similar expressions with the signs of the terms α_{xz} and α_{yz} changed when it is a rotation through ϕ followed by a reflection. From these relations it may easily be shown that

$$\chi'\ (\mathrm{R}) = 2 \cos\phi_{\mathrm{R}}\ (\pm 1 + 2 \cos\phi_{\mathrm{R}})$$

the plus or the minus sign being used according as R is a pure rotation or a

rotation reflection. The selection rule relating to a normal co-ordinate belonging to the irreducible representation Γ_i will now be written as

$$\left.\begin{matrix} \\ \end{matrix}\right\} \begin{matrix} = 0 \cdots \text{inactive} \\ \neq 0 \cdots \text{active} \end{matrix} \qquad \sum_R 2 \cos \phi_R (\pm 1 + 2 \cos \phi_R) \chi_i (R) \qquad (3)$$

2. *First Overtones.*—The selection rules that are appropriate to the various overtones may be derived by similar methods. Tisza has made a very complete study of these cases and the details need not be repeated here. It may however be mentioned that lines of higher order are of very infrequent occurrence in Raman effect and the few cases that have been observed are limited to the first overtones. The intensity of the higher overtones is so very small that a consideration of these is not of much practical importance. We will accordingly confine our discussion to the first overtones only and quote the results of Tisza. Relation (4) gives C_i, the number of times the first overtone of a normal mode coming under a certain irreducible representation occurs in any irreducible representation Γ_i of the group

$$C_i = \frac{1}{N} \sum_R \chi^2 (R) \chi_i (R). \qquad (4)$$

In equation (4)

$$\chi^2 (R) = \frac{[\chi (R)]^2 + \chi (R^2)}{2}.$$

By applying the test contained in equation (4) to all the irreducible representations of the group of symmetry operations, complete information as to the various types under which an overtone comes may easily be obtained. If all or some of these types are active, then the overtone is also active. If all the constituents are inactive, then the overtone is also inactive.

3. *Combinations.*—Combinations are also of infrequent occurrence in Raman effect and we need consider only the simple case of the fundamental of one normal mode combining with the fundamental of another normal mode. The two modes that are combining may or may not belong to the same irreducible representation. Tisza has given the general theory and his result, simplified so as to be applicable to this case will be given here. Equation (5) gives C_i, the number of times a combination between two normal modes, one coming under the irreducible representation (k) and the other coming under (l), occurs in any irreducible representation Γ_i of the group

$$C_i = \frac{1}{N} \sum_R \chi^{(kl)}(R) \chi_i (R). \qquad (5)$$

In equation (5)

$$\chi^{(kl)} (R) = \chi^{(k)} . \chi^{(l)}.$$

The expression is valid both when (l) is the same as (k) and different from (k). Proceeding in a manner similar to that adopted in the case of the overtones, we can express the combination as the sum of several types of motion coming

under different irreducible representations. If all or some of these types are active, then the combination is also active and if all the constituents are inactive, then the combination is also inactive.

4. *Some Special Cases.*—We will now give a number of theorems relating to certain special cases :

1. *All modes of oscillation coming under the total symmetric class are always Raman active.*—Since the character χ_i (R) is 1 for all R for a total symmetric class by definition, it is easily seen from (3) that we have to show that

$$\sum_R 2 \cos \phi_R \ (\pm 1 + 2 \cos \phi_R) \neq 0$$

for all groups of symmetry operations in order to prove the above theorem. Various groups listed by Tisza, irrespective of whether they are of crystallographic significance or not, have been considered by us and in all cases the above relation has been found to hold good. The details will be omitted here as they consist in merely summing up various trigonometrical series but it may be stated that in all cases the sum has been found to be a multiple of N, the order of the group, as may be expected.

2. *The first overtone of every normal mode is Raman active irrespective of whether the fundamental itself is active or not.*—Since we have already proved that the total symmetric oscillation is always Raman active, in order to prove this theorem we need only show that all first overtones occur at least once in the total symmetric irreducible representation. An inspection of (4) reveals that this is achieved if we prove that

$$\sum_R \chi^2 (R) \neq 0.$$

For all non-degenerate oscillations the character is either $+1$ or -1 for all R and $[\chi (R)]^2$ as well as $\chi (R^2)$ reduce to $+1$ for all R and the above relation is at once satisfied. In fact, the representation of such overtones is equivalent to the irreducible representation of the total symmetric type itself. In the case of degenerate oscillations, the proof is slightly more complicated and depends on the following theorem

$$\sum_R [\chi (R)]^2 = N.$$

In order that $\sum_R \chi^2 (R)$ may be zero, we should have $\sum_R \chi (R^2)$ equal to $-N$ which is never the case. Thus the overtone contains at least one component coming under the total symmetric class.

3. We may now go further and conclude that *if we are dealing with liquids or gases in which the molecules are oriented at random, the overtones may exhibit a depolarisation factor less than 6/7 irrespective of whether the Raman line due to the fundamental is polarised or depolarised.*

4. *If a centre of inversion is one of the elements in the group, all normal modes which are antisymmetric with respect to it are Raman inactive.* For every

operation R which has the character χ_i (R) there is an operation R_i obtained by combining i with R having the character $-\chi_i$ (R) in all irreducible representations which are antisymmetric with respect to i. This combination can be regarded as R followed by a rotation reflection through π. If in the representation defined by the tensor components, the character of R is $2\cos\phi_R\ (\pm 1 + 2\cos\phi_R)$ then the character of R_i is $2\cos\ (\phi_R + \pi)\ (\mp 1 + 2\cos\phi_{R+\pi})$ which is the same as $2\cos\phi_R\ (\pm 1 + 2\cos\phi_R)$. Consequently $\sum_R 2\cos\phi_R\ (\pm 1 + 2\cos\phi_R)\ \chi_i$ (R) vanishes, the terms cancelling in pairs and the mode is inactive.

5. *All normal modes which are symmetric with respect to a centre of inversion are infra-red inactive.*

This theorem may be proved in a manner analogous to the foregoing one by studying the behaviour of the character $\pm 1 + 2\cos\phi_R$ in the representation defined by the vector components.

6. *If a group possessing a p-gonal symmetry has a plane of reflection σ_h as one of its elements, it follows that a centre of inversion is also an element when p is even and the foregoing rule applies as such.*

7. *The sum $\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$ exists only in the total symmetric class. This has the consequence of giving a depolarisation value of 6/7 for all the Raman lines coming under any of the irreducible representations with the exception of the total symmetric class in the case of liquids and gases.*

Since $\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$ is an invariant for all R, its character is always 1 and therefore it comes only under the total symmetric class. By virtue of the orthogonality relations, it does not come in any other representation.

8. *All Raman active normal modes combine with each one of the modes coming under the total symmetric class to give Raman active combination tones. On the other hand, the combination of an inactive mode with a mode belonging to the total symmetric class is also inactive.* This follows from the fact that the characters of the combination of any mode with one coming under the total symmetric class remain the same as those of the original itself.

VI. Cubic Crystals[12]

Diamond and Rock Salt.—The diamond arrangement and the sodium chloride arrangement are very frequently met with in this class of crystals.

[12] In the following sections, if specific references are not indicated, it is to be presumed that the experimental data in respect of Raman effect are taken from *Landolt Bornstein Tabellen*. The infra-red data are taken from *Das Ultrarote Spektrum* by Schæfer and Matossi. In both cases, the frequencies are given as wave-numbers per cm. The crystal structures are mostly obtained from *The Structure of Crystals* by Wyckoff.

Special interest also attaches to these two substances as their Raman spectra have been studied with great care by a number of investigators. It may easily be shown[13] that there is only one triply degenerate normal oscillation to be considered in each of these two cases. In the case of diamond, this may be pictured as a to and fro motion against each other of the two interpenetrating lattices. In the case of rock salt, one portion of the lattice consisting of the sodium atoms alone oscillates against the other consisting of the chlorine atoms. The location of the centre of symmetry is different in the two cases and this results in the normal oscillation becoming symmetric with respect to the centre in diamond and anti-symmetric with respect to it in rock salt. We should accordingly expect a strong Raman line in diamond with no corresponding absorption in the infra-red and a strong infra-red absorption in rock salt with no corresponding Raman line. It is well known that the experimental results which have been obtained at a very early stage in the history of the subject are in full agreement with these conclusions.

A better physical picture of this interesting difference between the two types of crystals coming under the same class may be obtained by referring to Fig. 1.

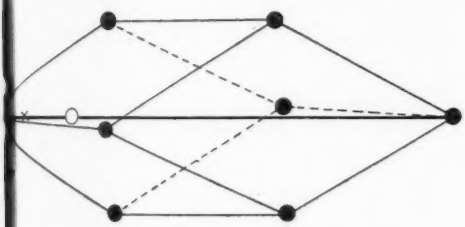


Fig. 1 a

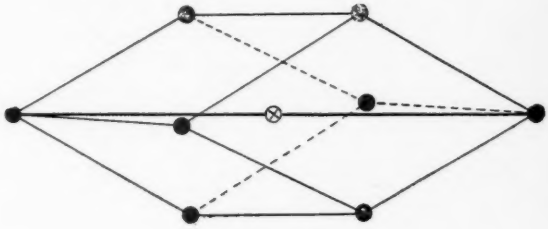


Fig. 1 b.

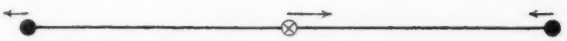


Fig. 1 c.

In Fig. 1 *a* (diamond), all atoms denoted by dots belong to one lattice and that denoted by a circle belongs to the other. The location of the centre of symmetry is shown by a cross and it is easily seen that a mutual oscillation of the two lattices which is symmetric with respect to the centre resembles the only normal oscillation of a diatomic molecule and is accordingly Raman active. In Fig. 1 *b* (rock salt), same notation is employed and it is easily

[13] T. Venkatarayudu, *Proc. Ind. Acad. Sci.*, (A), 1938, **8**, 349.

seen that the location of the centre is such that the normal oscillation is antisymmetric with respect to it. This resembles one of the normal modes of a linear symmetrical triatomic molecule shown in Fig. 1 *c*, and is accordingly Raman inactive and infra-red active. Crystals like those of KCl, KBr, etc., which have the NaCl structures will be expected to behave similarly and exhibit no Raman lines, whereas crystals of ZnS, AgI and all others having the diamond arrangement may be expected to behave like diamond.

VII. Trigonal Crystals

1. *Calcite and Sodium Nitrate.*—These two substances have the same crystal structures and exactly similar considerations apply to both. The space group is D_{3d}^6. The unit cell which is shown in Fig. 2 is an elongated rhombohedron and contains two molecules. The lattices are ionic and consist of the CO_3 ion and the metal ion in each case. The co-ordinates of the atoms are

Ca (1, 2) : $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{3}{4}\frac{3}{4}\frac{3}{4}$

C (3, 4) : $0\,0\,0$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

O (5 to 10) : $\omega\ \bar{\omega}\ 0$; $\bar{\omega}\ 0\ \omega$; $0\ \omega\ \bar{\omega}$;

$\frac{1}{2} - \omega, \omega + \frac{1}{2}, \frac{1}{2}$; $\omega + \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, -\omega$; $\frac{1}{2}, \frac{1}{2} - \omega, \omega + \frac{1}{2}$

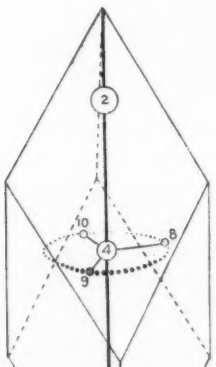


FIG. 2

The operations of this group are as follows :

E (Identity)

$2S_4^1$ {(1) (2) (3, 4) (5, 9, 7, 8, 6, 10)
{(1) (2) (3, 4) (5, 10, 6, 8, 7, 9)

$2C^1$ {(1) (2) (3) (4) (8, 10, 9) (5, 7, 6)
{(1) (2) (3) (4) (8, 9, 10) (5, 6, 7)

i (1) (2) (3, 4) (5, 8) (6, 9) (7, 10)

$3\sigma_v$ (glide) {(1,2) (3,4) (5,8) (6,10) (7,9)
{(1,2) (3,4) (5,10) (6,9) (7,8)
{(1,2) (3,4) (5,9) (6,8) (7,10)

$3C_2$ {(1,2) (3) (4) (5) (8) (6,7) (9,10)
{(1,2) (3) (4) (6) (9) (5,7) (8,10)
{(1,2) (3) (4) (7) (10) (5,6) (8,9)

The character Table and the values of n_i, n_i', etc., are given below :

D_{3d}^6	E	$2S_4^1$	$2C^1$	i	$3\sigma_v$	$3C_2$	n_i	External T	External L	n_i'	Raman	Infra-red
A_1 ..	1	1	1	1	1	1	1	0	0	1	p	f
A_2 ..	1	1	1	1	−1	−1	3	0	2	1	f	f
B_1 ..	1	−1	1	−1	1	−1	4	1	2	1	f	p
B_2 ..	1	−1	1	−1	−1	1	2	0	1	1	f	f
E_1 ..	2	1	−1	−2	0	0	6	1	3	2	f	p
E_2 ..	2	−1	−1	2	0	0	4	0	2	2	p	f
ω_R ..	10	2	4	2	0	4						
$h_j\chi_i'$ ..	30	0	0	−6	0	−12						

The normal co-ordinates in respect of the various representations are given below. The co-ordinate system chosen is such that the positive Z- and the X-axes are respectively parallel to the lines joining the atoms 3, 1 and 3, 5. The Y-axis is so chosen that the co-ordinate system becomes a right-handed one, m_1, m_2 and m_3 are respectively the masses of the calcium, carbon and oxygen atoms. Corresponding to the 10 atoms (30 degrees of freedom) in the unit cell we get 9 single modes, 9 doubly degenerate modes and 1 single translation and one doubly degenerate translation. Of these, 4 single and 4 degenerate modes are internal to the CO_3 ion (see Fig. 3*a*).

$$Q_1\,(i) = 2(x_5 - x_8) - (x_6 + x_7 - x_9 - x_{10}) - \sqrt{3}\,(y_6 - y_7 - y_9 + y_{10}) \quad A_1$$

$$\left.\begin{aligned} Q'_2\,(L) &= m_3(z_3 - z_4) + m_2(z_5 + z_6 + z_7 - z_8 - z_9 - z_{10}) \\ Q'_3\,(i) &= 3(z_3 - z_4) - (z_5 + z_6 + z_7 - z_8 - z_9 - z_{10}) \\ Q'_4\,(L) &= 2(y_5 - y_8) - (y_6 + y_7 - y_9 - y_{10}) - \\ &\qquad \sqrt{3}\,(x_7 - x_{10} - x_6 + x_9) \end{aligned}\right\} \quad .. A_2$$

$$\left.\begin{aligned} Q_z\,(T) &= z_1 + z_2 + z_3 + z_4 + z_5 + z_6 + z_7 + z_8 + z_9 + z_{10} \\ Q'_5\,(L) &= 2(y_5 + y_8) - (y_7 + y_{10} + y_6 + y_9) - \\ &\qquad \sqrt{3}\,(x_7 + x_{10} - x_6 - x_9) \\ Q'_6\,(i) &= 3m_3(z_3 + z_4) - m_2(z_5 + z_6 + z_7 + z_8 + z_9 + z_{10}) \\ Q_7\,(L) &= (m_2 + 3m_3)(z_1 + z_2) - m_1(z_3 + z_4 + z_5 + z_6 + z_7 \\ &\qquad + z_8 + z_9 + z_{10}) \end{aligned}\right\} \quad .. B_1$$

$$\left.\begin{aligned} Q'_8\,(i) &= 2(x_5 + x_8) - (x_6 + x_7 + x_9 + x_{10}) - \sqrt{3}\,(y_6 - y_7 + y_9 - y_{10}) \\ Q'_9\,(L) &= z_1 - z_2 \end{aligned}\right\} \quad .. B_2$$

$$\left.\begin{aligned} Q_x\,(T) &= x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8 + x_9 + x_{10} \\ Q_y\,(T) &= y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9 + y_{10} \\ Q'_{10a}\,(L) &= 2(z_5 + z_8) - z_6 - z_7 - z_9 - z_{10} \\ Q'_{11a}\,(i) &= 2(x_5 + x_8) - (x_6 + x_7 + x_9 + x_{10}) \\ &\qquad + \sqrt{3}\,(y_6 - y_7 + y_9 - y_{10}) \\ Q'_{12a}\,(L) &= x_1 - x_2 \\ Q'_{13a}\,(i) &= 3m_3(x_3 + x_4) - m_2(x_5 + x_6 + x_7 + x_8 + x_9 + x_{10}) \\ Q'_{14a}\,(L) &= (m_2 + 3m_3)(x_1 + x_2) \\ &\qquad - m_1(x_3 + x_4 + x_5 + x_6 + x_7 + x_8 + x_9 + x_{10}) \\ Q'_{10b} &= z_7 - z_6 - z_9 + z_{10} \\ Q'_{11b} &= 2(y_5 + y_8) - y_6 - y_7 - y_9 - y_{10} \\ &\qquad - \sqrt{3}\,(x_6 - x_7 + x_9 - x_{10}) \\ Q'_{12b} &= y_1 - y_2 \\ Q'_{13b} &= 3m_3(y_3 + y_4) - m_2(y_5 + y_6 + y_7 + y_8 + y_9 + y_{10}) \\ Q'_{14b} &= (m_2 + 3m_3)(y_1 + y_2) \\ &\qquad - m_1(y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9 + y_{10}) \end{aligned}\right\} \quad .. E_1$$

$$\left.\begin{aligned} Q'_{15a}\,(L) &= 2(z_5 - z_8) - z_6 - z_7 + z_9 + z_{10} \\ Q'_{16a}\,(i) &= 2(x_5 - x_8) - (x_6 + x_7 - x_9 - x_{10}) + \sqrt{3} \\ &\qquad (y_6 - y_7 - y_9 + y_{10}) \\ Q'_{17a}\,(L) &= m_3(x_3 - x_4) + m_2(x_5 - x_8 + x_7 - x_{10} + x_6 - x_9) \\ Q'_{18a}\,(i) &= 3(x_3 - x_4) - (x_5 + x_6 + x_7 - x_8 - x_9 - x_{10}) \\ Q'_{15b} &= z_7 + z_9 - z_6 - z_{10} \\ Q'_{16b} &= 2(y_5 - y_8) - y_6 - y_7 + y_9 + y_{10} \\ &\qquad - \sqrt{3}\,(x_6 - x_7 - x_9 + x_{10}) \\ Q'_{17b} &= m_3(y_3 - y_4) + m_2(y_5 - y_8 + y_7 - y_{10} + y_6 - y_9) \\ Q'_{18b} &= 3(y_3 - y_4) - (y_5 - y_8 + y_7 - y_{10} + y_6 - y_9) \end{aligned}\right\} \quad .. E_2$$

Fig. 3 *a* contains a diagrammatic representation of all the internal modes whereas Fig. 3 *b* refers to the external modes. In the case of degenerate modes, only those having the suffix *a* are given. The figures show very

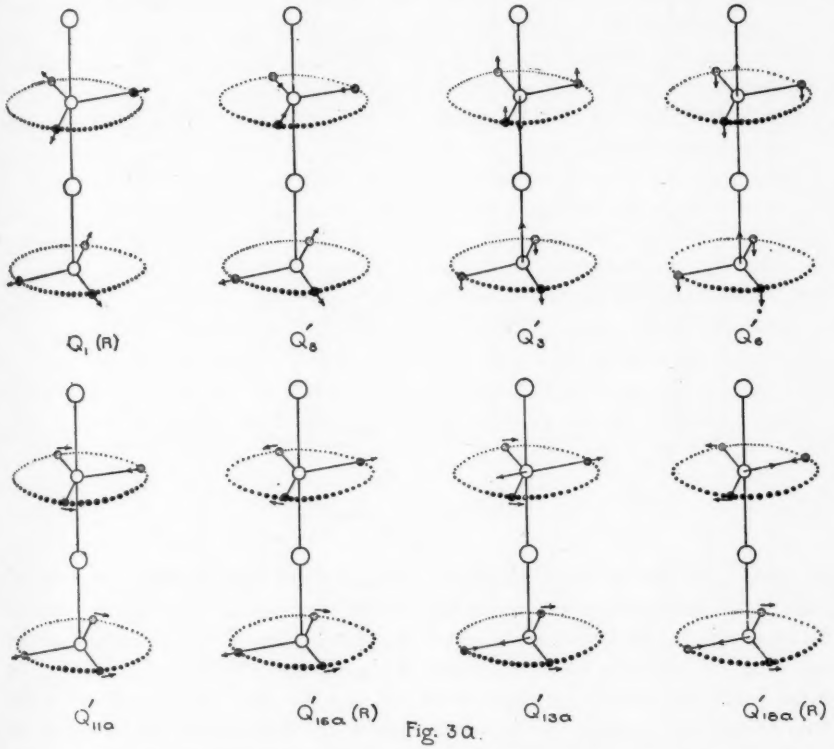


Fig. 3 a.

clearly the relationship between the normal modes of a free CO_3 ion and those of the crystal. The translations and rotations of one of the CO_3 groups in the crystal combine with the corresponding translations and rotations of the other to give the various external modes. For example Q_2 and Q_2' constitute a pair arising from the combination of translations of the free ion along Z. Similarly Q'_{10a} and Q'_{15a} constitute a pair arising from the combination of rotations of the free ion about the Y-axis. Other pairs are given side by side in Fig. 3 *b*.

The free CO_3 ion is well known to have two single (ν_1 and ν_2) and two doubly degenerate (ν_3 and ν_4) internal normal modes. ν_1 represents the total symmetric oscillation and is Raman active and infra-red inactive.

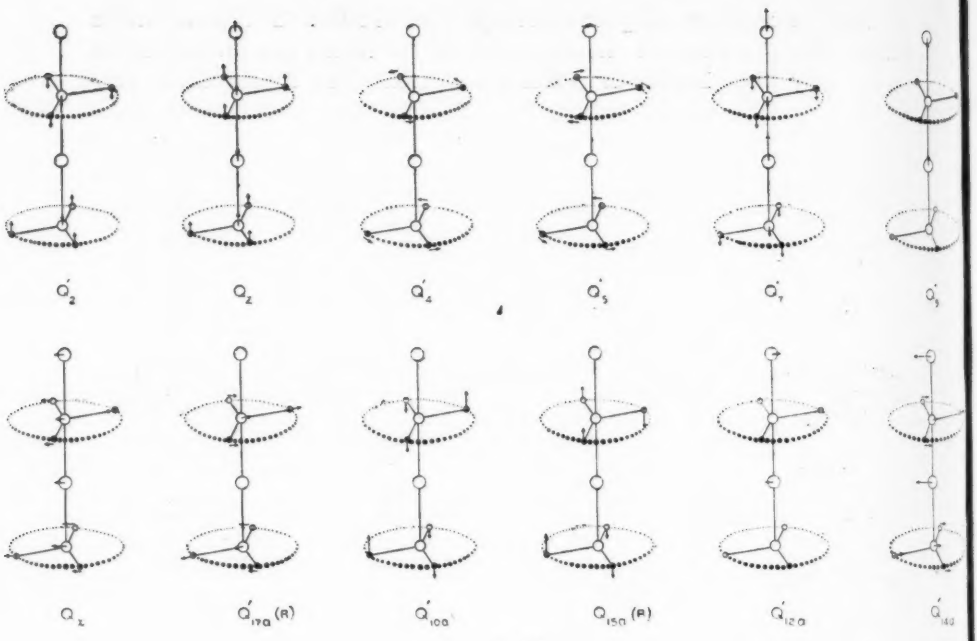


Fig. 3*b*

ν_2 represents the mode in which the central atom moves along the trigonal axis and is Raman inactive and infra-red active. ν_3 and ν_4 are active in both Raman effect and infra-red absorption. Each one of these normal modes again splits into two internal modes of the crystal. Q_1 and Q_8' of Fig. 3*a* arise from the total symmetric mode of the free ion. In the former, the two groups are moving in phase whereas in the latter they are moving out of phase. Similarly Q_3' and Q_6' arise from the second non-degenerate mode of the free ion in which the Z co-ordinate alone varies. Q'_{11a} and Q'_{18a} form one pair and Q'_{13a} and Q'_{18a} form the other pair corresponding to the two doubly degenerate normal modes of the free ion.

The experimental results in respect of calcite are contained in Tables I and II. One or two very weak lines said to have been recorded by certain observers are omitted as their reality is somewhat doubtful. Since the Raman active and infra-red inactive total symmetric oscillation of the CO_3 ion splits into two modes one of which comes under A_1 (Raman active and infra-red inactive) and the other under B_2 (inactive in both), we should expect only one line corresponding to these modes in the crystal. Accordingly we obtain only one line at 1087 in the Raman spectrum of calcite

(see Table I) which is not represented in the infra-red absorption. The second non-degenerate mode of the free ion which is inactive in Raman effect and active in the infra-red splits into two which come under A_2 (inactive in both) and B_1 (Raman inactive and infra-red active). Accordingly we do not get any Raman line in the crystal corresponding to the infra-red absorption at 879. The two doubly degenerate modes of the free ion, both of which are active in the Raman effect as well as infra-red absorption, continue to be degenerate in the crystal but split into four modes and come under the representations E_1 and E_2 with slightly altered selection rules. It may be noticed that whereas we should expect an exact coincidence between the measurements in the Raman effect and in infra-red absorption for the free-ion in respect of this pair of frequencies, we should anticipate a departure in the case of the crystal. The observed values for calcite crystal are 714 and 1432 in Raman effect (E_2) and 706 and 1429 to 1492 in infra-red absorption (E_1). The differences are not very appreciable and this enables us to conclude that the doubling arising out of the fact that the basis contains more than one free ion is not of much consequence.[14] In addition to these lines, calcite shows a weak line at 1749 which is to be regarded as an overtone of B_1.

TABLE I

Raman Frequencies

Crystal	Lattice		Internal				Overtone
	E_2	E_2	E_2	B_1	A_1	E_2	$2B_1$
Calcite ..	156	283	714	..	1087	1432	1749
	5d	1d	0		50	2	1
$NaNO_3$ ..	100	189	726	..	1068	1385	1670
	2	4d	2		8	4	0

TABLE II

Infra-red Frequencies

Crystal	Lattice					Internal			
	Ordinary (E_1)			Extra-ord. (B_1)		E_1	B_1	A_1	E_1
Calcite ..	106	182	330	106	357	706	879	..	1429 to 1492
$NaNO_3$ ..	71	133	217	71	217	692	831	..	1405

[14] Some of these conclusions have been briefly described by Placzek, *The Structure of Molecules*, 1932, p. 65.

The results contained in the character Table show that we should expect 2 lattice oscillations (Q'_{15a} and Q'_{17a}) in Raman effect and five lattice oscillations (Q_5', Q_7', Q'_{10a}, Q'_{12a}, Q'_{14a}) in infra-red absorption, there being no correspondence between the two spectra. We accordingly obtain two Raman lines at 156 and 283 in calcite. In the infra-red spectrum we obtain 106, 182 and 330 when the absorption relates to the ordinary ray and 106 and 357 again when the absorption relates to the extraordinary ray. The two latter are to be counted as distinct and coming under the class B_1. It may be seen from the curves reproduced on page 357 of Schæfer and Matossi's book already referred to that 357 is quite distinct from 330.

The case of sodium nitrate is exactly similar to that of calcite. The experimental results are tabulated along with those of calcite in Tables I and II. The pair at 726 and 1385 of the Raman spectrum may be compared with 692 and 1405 of the infra-red absorption. For reasons already stated, there should be no exact coincidences between these pairs and it may be noted that the differences in this case are slightly more marked than in the case of calcite.

2. *Corundum.*—This substance (Al_2O_3) crystallises with the same space group as calcite and has a similar structure. The unit cell (Fig. 4) is

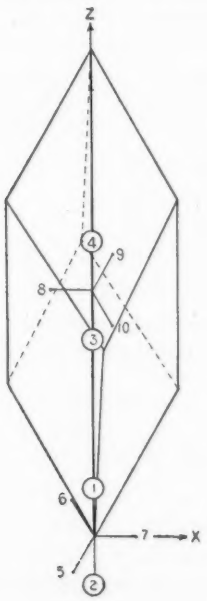


FIG. 4

a rhombohedron containing two molecules. The lattice is molecular as the Al_2O_3 molecules may be definitely isolated. The co-ordinates of the atoms are :

Al (1 to 4) : $\omega\ \omega\ \omega$; $\bar{\omega}\ \bar{\omega}\ \bar{\omega}$; $\frac{1}{2}-\omega, \frac{1}{2}-\omega, \frac{1}{2}-\omega$; $\frac{1}{2}+\omega, \frac{1}{2}+\omega, \frac{1}{2}+\omega$.

0 (5 to 10) : $v\ \bar{v}\ 0$; $\bar{v}\ 0\ v$; $0\ v\ \bar{v}$; $\frac{1}{2}-v, \frac{1}{2}+v, \frac{1}{2}$; $\frac{1}{2}+v, \frac{1}{2}, \frac{1}{2}-v$; $\frac{1}{2}, \frac{1}{2}-v, \frac{1}{2}+v$.

The operations of the group are :

E

$2\ S_6^1$ (1, 3) (2, 4) (7, 10, 5, 8, 6, 9)
(1, 3) (2, 4) (7, 9, 6, 8, 5, 10)

$2\ C^1$ (1) (2) (3) (4) (5, 6, 7) (8, 9, 10)
(1) (2) (3) (4) (5, 7, 6) (8, 10, 9)

i (1, 3) (2, 4) (5, 9) (6, 10) (7, 8)

$3\sigma_v$ (glide) (1, 4) (2, 3) (5, 10) (6, 9) (7, 8)
(1, 4) (2, 3) (5, 9) (6, 8) (7, 10)
(1, 4) (2, 3) (5, 8) (6, 10) (7, 9)

$3C_2$ (7) (8) (1, 2) (3, 4) (5, 6) (9, 10)
(5) (9) (1, 2) (3, 4) (6, 7) (8, 10)
(6) (10) (1, 2) (3, 4) (5, 7) (8, 9)

The corresponding character Table along with the selection rules and other features is given below :

D_{3d}^6	E	$2S_6^1$	$2C^1$	i	$3\sigma_v$	$3C_2$	External n_i	T	L	n_i'	Raman	Infra-red
A_1 ..	1	1	1	1	1	1	2	0	0	2	p	f
A_2 ..	1	1	1	1	−1	−1	3	0	2	1	f	
B_1 ..	1	−1	1	−1	1	−1	3	1	1	1	f	p
B_2 ..	1	−1	1	−1	−1	1	2	0	0	2	f	f
E_1 ..	2	1	−1	−2	0	0	5	1	1	3	f	p
E_2 ..	2	−1	−1	2	0	0	5	0	2	3	p	f
ω_R	10	0	4	0	0	2						
$h_i\chi_i'$ ..	30	0	0	0	0	−6						

The trigonal axis is chosen as the Z-axis. The X-axis is shown in Fig. 4 and the Y-axis is so chosen as to make the system a left-handed one. m_1 and m_2 are respectively the masses of the aluminium and oxygen atoms. The normal co-ordinates run as follows :

$$
\left.\begin{aligned}
Q_1'\,(i) &= m_2(z_1 - z_2 - z_3 + z_4) - m_1[(x_5 + x_6 - x_9 - x_{10}) \\
&\quad - 2(x_7 - x_8) - \sqrt{3}\,(y_5 - y_6 - y_9 + y_{10})] \\
Q_2'\,(i) &= 6(z_1 - z_2 - z_3 + z_4) + (x_5 + x_6 - x_9 - x_{10}) \\
&\quad - 2(x_7 - x_8) - \sqrt{3}\,(y_5 - y_6 - y_9 + y_{10})]
\end{aligned}\right\} A_1
$$

$$
\left.\begin{aligned}
Q_3'\,(L) &= (y_5 + y_6 - y_9 - y_{10}) - 2(y_7 - y_8) \\
&\quad + \sqrt{3}\,(x_5 - x_6 - x_9 + x_{10}) \\
Q_4'\,(L) &= z_1 + z_2 + z_5 + z_6 + z_7 - z_3 - z_4 - z_8 - z_9 - z_{10} \\
Q_5'\,(i) &= 3m_2(z_1 + z_2 - z_3 - z_4) - 2m_1(z_5 + z_6 + z_7 - z_8 - \\
&\quad z_9 - z_{10})
\end{aligned}\right\} A_2
$$

$$
\left.\begin{aligned}
Q_x\,(T) &= x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8 + x_9 + x_{10} \\
Q_y\,(T) &= y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9 + y_{10} \\
Q'_{10a}\,(i) &= 3m_2(x_1 + x_2 + x_3 + x_4) \\
&\quad - 2m_1(x_5 + x_6 + x_7 + x_8 + x_9 + x_{10}) \\
Q'_{11a}\,(i) &= (x_1 - x_2 + x_3 - x_4) + \tfrac{1}{3}(2z_7 + 2z_8 - z_5 - z_6 - z_9 - z_{10}) \\
Q'_{12a}\,(L) &= m_2(x_2 - x_1 + x_4 - x_3) \\
&\quad + m_1(2z_7 + 2z_8 - z_5 - z_6 - z_9 - z_{10}) \\
Q'_{13a}\,(i) &= 2(x_7 + x_8) - (x_5 + x_6 + x_9 + x_{10}) \\
&\quad - \sqrt{3}\,(y_5 - y_6 + y_9 - y_{10}) \\
Q'_{10b} &= 3m_2(y_1 + y_2 + y_3 + y_4) \\
&\quad - 2m_1(y_5 + y_6 + y_7 + y_8 + y_9 + y_{10}) \\
Q'_{11b} &= (y_1 - y_2 + y_3 - y_4) + (z_5 - z_6 + z_9 - z_{10}) \\
Q'_{12b} &= m_2(y_2 - y_1 + y_4 - y_3) + m_1(z_5 - z_6 + z_9 - z_{10}) \\
Q'_{13b} &= 2(y_7 + y_8) - (y_5 + y_6 + y_9 + y_{10}) \\
&\quad + \sqrt{3}\,(x_5 - x_6 + x_9 - x_{10})
\end{aligned}\right\} E_1
$$

Q_6' (L), Q_z (T), Q'_7 (i) coming under B_1 are obtained from those given under A_2 by changing the signs of the terms having the suffixes 3, 4, 8, 9 and 10. Q_8' (i) and Q_9' (i) coming under B_2 are obtained in a similar manner from those given under A_1. Q'_{14a} (L), Q'_{15a} (i), Q'_{16a} (i), Q'_{17a} (L), and Q'_{18a} (i) and the b components that are degenerate with these coming under E_2 are likewise obtained from the co-ordinates given under E_1. Thus we may write down all the 20 normal co-ordinates inclusive of (Q_x, Q_y) and Q_z. In classifying the normal co-ordinates as external and internal, the group Al_2O_3 is taken as one unit as it is known from X-ray analysis that the lattice is molecular. The case of the free Al_2O_3 molecule has also been worked out[15] by us and found to exhibit besides the pure rotations and translations,

[15] The details are not given in this paper for want of space.

2 total symmetric oscillations (A_1), one single mode in which the Z components alone vary (B_1) and three doubly degenerate modes (E_1 and E_2) corresponding to the nine internal degrees of freedom. As in the case of calcite, in the place of the three doubly degenerate modes of Al_2O_3, we get six doubly degenerate modes (Q'_{10}, Q'_{11}, Q'_{13}, Q'_{15}, Q'_{16}, Q'_{18}) in the crystal. The 2 total symmetric oscillations give place to 4, two of them (Q_1' and Q_2') coming under A_1 and the other two (Q_8' and Q_9') coming under B_2. The single mode in which the Z components alone vary gives rise to two modes, one (Q_5') under A_2 and the other (Q_7') under B_1. The total number of internal degrees of freedom is 18. The normal co-ordinates corresponding to the pure rotations and translations of the isolated Al_2O_3 molecule combine in a like manner to give all the external modes of the crystal.

It will be seen from the character Table that we should expect the Raman spectrum of this crystal to consist of 2 lines of the total symmetric class and 3 lines of the class E_2 so far as the internal oscillations are concerned. Two frequencies at 931 and 1191 have actually been observed and these are presumably to be identified with the total symmetric oscillations. No lines have been recorded which may be classed under E_2. We should also expect 2 lattice oscillations of the same class E_2 to be recorded in the Raman spectrum but the available data do not show any. These may be very weak as they involve relative motions between the aluminium and oxygen atoms. A more careful study of the Raman spectrum of this crystal is nevertheless desirable.

VIII. Raman Spectrum and Different Crystalline Modifications

1. *Aragonite.*—This case is of great interest as it differs from calcite only in having a different crystal structure. The space group is V_h^{16}. The unit cell, a projection of which is shown in Fig. 5, contains four molecules

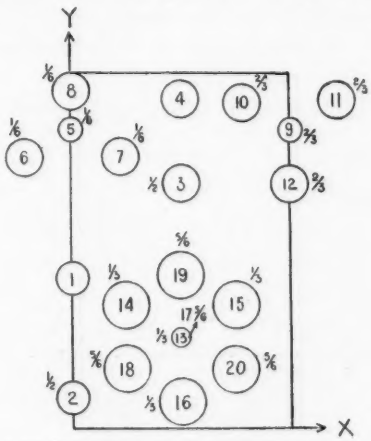


FIG. 5

of $CaCO_3$. The lattice is ionic and is composed of the CO_3 and the metal ions. The co-ordinates of the atoms are

Ca (1 to 4) : $0, \frac{5}{12}, 0$; $\frac{1}{2}. -\frac{5}{12}, \frac{1}{2}$; $0, \frac{1}{12}, \frac{1}{2}$; $\frac{1}{2}, \frac{11}{12}, 0$

C (5, 9, 13, 17) : $0, \frac{3}{4}, \frac{1}{6}$; $\frac{1}{2}, \frac{1}{4}, \frac{1}{3}$; $0, \frac{3}{4}, \frac{2}{3}$; $\frac{1}{2}, \frac{1}{4}, \frac{5}{6}$

O (6, 7, 8, 10, 11, 12, 14, 15, 16, 18, 19, 20) : $x\,y\,z$; $x+\frac{1}{2}, \bar{y}, \frac{1}{2}-z$; $x, \frac{1}{2}-y, z+\frac{1}{2}$; $\frac{1}{2}-x, y+\frac{1}{2}, \bar{z}$; $\bar{x}\,y\,z$; $\frac{1}{2}-x, y, \frac{1}{2}-z$; $x+\frac{1}{2}, y+\frac{1}{2}, \bar{z}$; $x, \frac{1}{2}-y, z+\frac{1}{2}$; $0\,q\,r$; $\frac{1}{2}, \bar{q}, \frac{1}{2}-r$; $0, \frac{1}{2}-q, \frac{1}{2}+r$; $\frac{1}{2}, \frac{1}{2}+q, \bar{r}$.

The operations of this group are as follows :

E

C^1 (Screw) (1, 3) (2, 4) (5, 13) (6, 14) (7, 15) (8, 16) (9, 17) (10,18) (11, 20) (12, 19)

C_2 (Screw) (1, 4) (2, 3) (5, 17) (6, 20) (7, 18) (8, 19) (9, 13) (10, 15) (11, 14) (12, 16)

C_2' (Screw) (1, 2) (3, 4) (5, 9) (6, 11) (7, 10) (8, 12) (13, 17) (14, 20) (15, 18) (16, 19)

i (1, 3) (2, 4) (5, 13) (6, 15) (7, 14) (8, 16) (9, 17) (10, 20) (11, 18) (12, 19)

σ_h (1) (2) (3) (4) (5) (8) (9) (12) (13) (16) (17) (19) (6, 7) (10, 11) (14, 15) (18, 20)

σ_v (glide) (1, 2) (3, 4) (5, 9) (6, 10) (7, 11) (8, 12) (13, 17) (14, 18) (15, 20) (16, 19)

σ_v' (glide) (1, 4) (2, 3) (5, 17) (6, 18) (7, 20) (8, 19) (9, 13) (10, 14) (11, 15) (12, 16)

The character Table is given below :

V_h^{16}	E	C^1	C_2	C_2'	i	σ_h	σ_v	σ_v'	External n_i	T	L	n_i'	Raman	Infra-red
A_{1g} ..	1	1	1	1	1	1	1	1	9	0	5	4	p	f
A_{2g} ..	1	−1	1	−1	1	−1	1	−1	6	0	4	2	p	f
B_{1g} ..	1	1	−1	−1	1	1	−1	−1	9	0	5	4	p	f
B_{2g} ..	1	−1	−1	1	1	−1	−1	1	6	0	4	2	p	f
A_{1u} ..	1	1	1	1	−1	−1	−1	−1	6	0	4	2	f	f
A_{2u} ..	1	−1	1	−1	−1	1	−1	1	9	1	4	4	f	p
B_{1u} ..	1	1	−1	−1	−1	−1	1	1	6	1	3	2	f	p
B_{2u} ..	1	−1	−1	1	−1	1	1	−1	9	1	4	4	f	p
u_R ..	20	0	0	0	0	12	0	0						
$h_j\chi_j'$ ..	60	0	0	0	0	12	0	0						

As there are 20 atoms in each unit cell and there is no degeneracy, we obtain 57 distinct normal modes in addition to the three pure translations. The normal co-ordinates have been obtained and classified into lattice and internal oscillations as shown in the previous table. As a full description of these will occupy a large amount of space, it will not be attempted here. A detailed study shows that firstly the two degenerate normal modes of the free CO_3 ion split into 4 non-degenerate modes thus making the total number 6 per each CO_3 group. When the crystal is taken as a whole, each of these further gives rise to four distinct normal modes resulting in 24 internal modes of oscillation for the aragonite crystal. These twenty-four internal modes are distributed amongst the various irreducible representations in the following manner. One component arising from each of ν_1, ν_2, ν_3 and ν_4 of the free ion appears in each of the representations A_{1g}, B_{1g}, A_2u and B_2u. Similarly one component arising from each of ν_3 and ν_4 only of the free ion appears in each of the representation A_{2g}, B_{2g}, A_1u and B_1u. ν_1, ν_2, ν_3 and ν_4 have the same significance as in calcite. This knowledge when combined with the selection rules given in the character Table for aragonite shows that its Raman spectrum should exhibit 2 components arising from ν_1, 2 from ν_2, 4 from ν_3 and 4 from ν_4. If as has already been noticed in the case of calcite, the splitting due to the multiplicity of groups in the basis of the crystal is not of much consequence, it follows that we should observe in the crystal only four lines corresponding to all the four normal frequencies ν_1, ν_2, ν_3 and ν_4 of the free ion. This result is of special significance and is in marked contrast with what has been obtained for calcite. While the mode corresponding to ν_2 cannot appear in the Raman spectrum of either the free ion or calcite, it is permitted to appear in the Raman spectrum of aragonite. The experimental results which are given in Table III are in accordance with such an expectation because a line at 852 which may be associated with ν_2 appears. 704, 1084 and 1460 are to be identified with ν_3, ν_1 and ν_4.

TABLE III

Raman and Infra-red Frequencies

Crystal	External									Internal			
Aragonite (Raman) ..	113	154	182	208	246	261				704	852	1084	1460
	2	10d	2	5	1	1				2	1	9	2
KNO_3 (Raman) ..	31	51	84							711	..	1049	1344
	0	4	8							0		6	2
Aragonite (Infra-red) ..	100	200	274	114	200	294	118	200	274	706 / 711	866	..	1492 / 1504
		b			*c*			*a*					

Other notable features in respect of the Raman spectrum of aragonite are as follows. While we should expect only two external oscillations in calcite to be Raman active, a much larger number are so in aragonite. Experimental results in fact show that there are about 6 components and some of them may even be capable of being resolved further. The infra-red absorption also shows an analogous complexity.

2. *Potassium Nitrate.*—KNO_3 is chemically similar to $NaNO_3$ but its crystal structure resembles that of aragonite. Between the crystals of KNO_3 and $NaNO_3$, there exists the same relationship as between the crystals of aragonite and calcite. The results obtained in KNO_3, which are also tabulated in Table III, should accordingly be exactly similar to those obtained in aragonite. It is apparent that a line at about 830 is to be expected in the KNO_3 crystal but has not yet been recorded. This line is forbidden in the Raman spectrum of the free NO_3 ion or the $NaNO_3$ crystal.

IX. Splitting of Degenerate Modes in Crystals of Lower Symmetry

Gypsum and Anhydrite.—We have already seen that the degenerate modes characterstic of the free CO_3 ion should be expected to split into several non-degenerate modes in the aragonite crystal owing to the absence of trigonal symmetry. This splitting may not however be appreciable as the symmetry of the aragonite crystal departs only to a small extent from the strictly hexagonal type. There are two interesting cases, namely, those of gypsum and anhydrite, which show this effect prominently and they will be dealt with here in some detail.[16] Gypsum belongs to the monoclinic class and has the space group C_{2h}^3 while anhydrite belongs to the orthorhombic class and has the space group V_h^{17}. There is no axis of a degree of symmetry higher than two-fold in either case and we should accordingly not expect any degenerate normal modes. The appropriate character Tables and the normal co-ordinates in these cases will not be reproduced here as the method of obtaining them has already been illustrated in the examples dealt with earlier. We will only state the results. The four distinct modes of oscillation appropriate to the free tetrahedral SO_4 group split into nine distinct modes in the crystals. These nine distinct modes undergo a further splitting on account of the fact that there are four such groups in each unit cell, thus giving an aggregate of 36 modes in each case. One or other of the four components coming from each one of the nine fundamental modes happens to be Raman active and we should accordingly expect both anhydrite and gypsum to exhibit all the nine components in their Raman spectra. It may be noted here that this result follows

[16] The main results in respect of these two crystals have been published by one of us in a preliminary communication. See *Proc. Ind. Acad. Sci.*, 1938, **8**, 345.

in spite of the fact that the SO_4 group preserves its tetrahedral symmetry in both gypsum and anhydrite and is not to be taken as indicating a departure from tetrahedral symmetry for the SO_4 ions in these crystals.

TABLE IV

Raman Frequencies

Substance	Lattice	Internal to SO_4 ion				Water bands
SO_4 ion ..	..	454 (ν_2) double	622 (ν_3) triple	983 (ν_1) single	1106 (ν_4) triple	..
$CaSO_4$ .. (Anhydrite)	126 169 233 (1) (2) (1)	415 499 (1) (5d)	609 628 674 (2) (2) (8)	1018 (15)	1108 1128 1160 (2) (10) (5)	..
$CaSO_4 \cdot 2H_2O$ .. (Gypsum)	..	414 494 (5) (3)	.. 618 672 (2b) (4)	1008 (20)	1113 1135 .. (2) (10)	3402 3493 (10d) (20)

The observed Raman frequencies in these crystals are given in Table IV. The case of the free SO_4 ion is included for comparison and the four normal modes corresponding to ν_1, ν_2, ν_3 and ν_4 are quite well known. The degree of degeneracy in these cases is indicated and the complete splitting that occurs in the crystals is interesting. The correspondence is quite obvious and the experimental results fully support the conclusions of the theory. The results in respect of gypsum suggest that one faint line in the neighbourhood of 600 and another in the neighbourhood of 1160 are yet to be recorded.

X. Comparison of the Raman Spectra of Free Molecules and the Corresponding Crystals

Mercurous Chloride.—This substance crystallises in the tetragonal system and possesses the space group D_{4h}^{17}. The unit cell contains two molecules of Hg_2Cl_2 and the lattice is molecular. Fig. 6 shows the arrangement of the

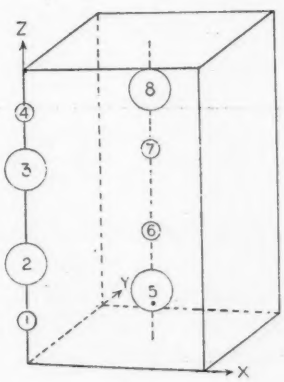


FIG. 6

atoms in the unit cell. The co-ordinates of the atoms are

Hg (1, 4, 6, 7) : $0\,0\,\omega$; $0\,0\,\bar{\omega}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - \omega$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + \omega$.

Cl (2, 3, 5, 8) : $0\,0\,v$; $0\,0\,\bar{v}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - v$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + v$.

The operations of the group are

E	
$2C^1$	(1) (2) (3) (4) (5) (6) (7) (8)
C^2	(1) (2) (3) (4) (5) (6) (7) (8)
$2C_2$	(14) (23) (58) (67)
$2C_2$	(14) (23) (58) (67)
i	(14) (23) (58) (67)
$2S^1$	(14) (23) (58) (67)
σ_h	(14) (23) (58) (67)
$2\sigma_v$	(1) (2) (3) (4) (5) (6) (7) (8)
$2\sigma_v'$	(1) (2) (3) (4) (5) (6) (7) (8)

The appropriate character Table and the selection rules are given below :

D_{4h}^{17}	E	$2C^1$	C^2	$2C_2$	$2C_2'$	i	$2S^1$	σ_h	$2\sigma_v$	$2\sigma_v'$	External n_i	T	L	n_i'	Raman	Infra-red
A_{1g}	1	1	1	1	1	1	1	1	1	1	4	0	0	4	p	f
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	0	0	0	0	..	..
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1	0	0	0	0	..	..
B_{2g}	1	−1	1	−1	1	1	−1	−1	−1	1	0	0	0	0	..	..
E_{1g}	2	0	−2	0	0	2	0	−2	0	0	4	1	1	2	p	f
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1	0	0	0	0	..	..
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	4	1	1	2	f	p
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1	0	0	0	0	..	..
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1	0	0	0	0	..	..
E_{1u} .. .	2	0	−2	0	0	−2	0	2	0	0	4	0	2	2	f	p
ω_R	8	8	8	0	0	0	0	0	8	8						
$h_i\chi_i'$	24	16	−8	0	0	0	0	0	16	16						

The axes chosen for representing the normal co-ordinates are shown in Fig. 6. m_1 and m_2 are respectively the masses of the mercury and chlorine atoms. Corresponding to the 24 degrees of freedom of the eight atoms in the unit cell, we get three pure translations, seven single and seven doubly degenerate modes. The normal co-ordinates are given below.

$$
\left.\begin{aligned}
Q_1'(i) &= m_2(z_1 - z_4 + z_6 - z_7) + m_1(z_2 - z_3 + z_5 - z_8).\\
Q_2'(i) &= m_2(z_1 - z_4 - z_6 + z_7) + m_1(z_2 - z_3 - z_5 + z_8)\\
Q_3'(i) &= (z_1 - z_4 - z_6 + z_7) - (z_2 - z_3 - z_5 + z_8)\\
Q_4'(i) &= (z_1 - z_4 + z_6 - z_7) - (z_2 - z_3 + z_5 - z_8)
\end{aligned}\right\} \quad A_{1g}
$$

$$
\left.\begin{aligned}
Q_x(\mathrm{T}) &= x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8\\
Q_y(\mathrm{T}) &= y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8\\
Q'_{5a}(\mathrm{L}) &= m_2(x_1 + x_4 - x_6 - x_7) + m_1(x_2 + x_3 - x_5 + x_8)\\
Q'_{6a}(i) &= (x_1 + x_4 - x_6 - x_7) - (x_2 + x_3 - x_5 - x_8)\\
Q'_{7a}(i) &= m_2(x_1 + x_4 + x_6 + x_7) - m_1(x_2 + x_3 + x_5 + x_8)\\
Q'_{5b} &= m_2(y_1 + y_4 - y_6 - y_7) + m_1(y_2 + y_3 - y_5 - y_8)\\
Q'_{6b} &= (y_1 + y_4 - y_6 - y_7) - (y_2 + y_3 - y_5 - y_8)\\
Q'_{7b} &= m_2(y_1 + y_4 + y_6 + y_7) - m_1(y_2 + y_3 + y_5 + y_8)
\end{aligned}\right\} \quad E_{1g}
$$

By altering the signs of terms with suffixes 3, 4, 7 and 8 in the normal coordinates occurring under A_{1g} we obtain Q_z and Q_8' (L), Q'_9 (i) and Q'_{10} (i) coming under A_{2u}. Similarly we obtain Q_{11a}' (L), Q_{12a}' (L), Q_{13a}' (i) and Q_{14a}' (i) and their b-components coming under E_{1u} from those given under E_{1g}. Ten of these are internal modes and their relationship to the normal oscillations of a free molecule will be clear from the following discussion.

The normal modes of a linear molecule of the type of Hg_2Cl_2 are well known and are shown in Fig. 7. The four internal oscillations coming under A_{1g} are akin to the total symmetric oscillations ν_1 and ν_2 and are Raman active.

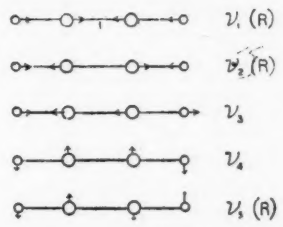


FIG. 7

Two others (Q'_{6a} and Q'_{7a}) which are in the degenerate class E_{1g} are akin to ν_4 and are also Raman active. The rest are similarly coming from ν_3 and ν_5 but are inactive in Raman effect. The interesting fact that while ν_4 is inactive in the Raman effect for a free molecule, oscillations similar to that become active in the case of a crystal may be noted. The reverse is the case for ν_5. If as in previous cases, we assume that the difference between the environments of the two molecules in the basis is not of much consequence, it is clear that we should expect only three Raman lines, two of the total symmetric class

A_{1g} and 1 of the degenerate class E_{1g}. Three strong lines at 165(6), 273(4), 295(1) have been observed in the Raman spectrum of Hg_2Cl_2 crystals. The last two may be identified with those coming under A_{1g} whereas the one at 165 may be identified with that coming under E_{1g}. An additional weak line at 320 has also been recorded and this is presumbly the overtone of the strong line at 165 or more probably the overtone of the analogous oscillation ν_5 the fundamental of which is forbidden in the Raman spectrum.

XI. Directional Excitation of Raman Lines in Crystals.

Calcite and Sodium Nitrate.—Since the selection rules in respect of the various tensor components are available individually, it is possible to study the nature of the scattered light for different orientations of a crystal. In view of the special importance of calcite, the results that are to be expected of it are given below along with the experimental results of Osborne[17] and of Schæfer, Matossi and Aderhold.[18] In the rectangular co-ordinate system OXYZ, light is always regarded as being incident along OX and the scattered light observed along OY, the XY-plane being horizontal. Table V contains the results for some of the possible orientations. The Raman spectrum of calcite consists of lines coming under only two representations, namely A_1 and E_2, and we need therefore consider only these two cases as all the lines of a given class will have the same polarisation characters. The results in

TABLE V

Directional Excitation

Incident light	Vibrations	Orientation of optic axis	ρ for 1087 (A_1)			ρ for 714 (E_2)			ρ for 283 (E_2)	
			T.	O.	S.M.A.	T.	O.	S.M.A.	O.	S.M.A.
Plane polarised ..	$\parallel^l$ to Z	$\parallel^l$ to X	0	0	..	0	1	..	4	..
,, ..	$\parallel^l$ to Y	,,	f	0	..	f	1	..	4	..
Unpolarised ..	YZ plane	,,	0	0	0	0	1	0	4	>1
Plane polarised ..	$\parallel^l$ to Z	$\parallel^l$ to Y	0	1	..	0	1	..	1	..
,, ..	$\parallel^l$ to Y	,,	f	f	..	f	f	..	1	..
Unpolarised ..	YZ plane	,,	0	1	<1	0	1	<1	1	<1
Plane polarised ..	$\parallel^l$ to Z	$\parallel^l$ to Z	0	0	..	f	>1	..	>1	..
,, ..	$\parallel^l$ to Y	,,	f	f	..	f	>1	..	<1	..
Unpolarised ..	YZ plane	,,	0	0	>1	f	5·6	>1	>2	>1

[17] *Dissertation*, University of Paris, 1932.
[18] *Z. f. Phys.*, 1930, **65**, 329.

the Table are applicable to the case of sodium nitrate crystals as well without any alteration.

The results given under the column, 'Theory' (T) apply only to the case where the specimen under examination is cut into the shape of a rectangular parallelopiped in such a way that a pair of opposite faces are normal to the optic axis. In this case, complications due to double refraction are eliminated and the results are rigorously correct. *f* denotes that both the horizontal and the vertical components have zero intensity individually. The considerable discrepancy that exists between the theory and experimental results may be noted and it is to be expected as it is quite conceivable that a cut crystal had not been used in these investigations. Even if a cut crystal is employed, it is very difficult to confine the incident and scattered rays in practice to specific directions. Deviations that are bound to occur will give rise to abnormal depolarisation values. If in addition to this, the incidence is not normal on the crystal faces, the ordinary and extraordinary beams travelling in different directions in the crystal cause complications. In view of these experimental difficulties, the exact significance of the values quoted from Osborne and Schæfer, Matossi and Aderhold is somewhat doubtful. There is a great field for more detailed investigations on these lines in cases where large single crystals of suitable shape can be obtained.

XII. Some General Remarks

From a close examination of the results contained in the previous pages, we are enabled to draw the following general conclusions. When a group of atoms constituting an ion or a molecule forms part of the unit cell of a crystal, its normal modes will in general undergo modification in three directions. The most important modification is in respect of the degenerate modes. They continue to be degenerate in the crystal as well, only when the crystal possesses the same order of symmetry as the free ion or the molecule. If the symmetry breaks down, the degeneracy also disappears and each degenerate mode will split and give rise to the appropriate number of distinct modes. For example, the SO_4 ion having a tetrahedral symmetry in the free state has two triply degenerate and one doubly degenerate normal modes. When a monoclinic $CaSO_4$, $2H_2O$ crystal or an orthorhombic $CaSO_4$ crystal (anhydrite) is built out of them, the tetrahedral symmetry has disappeared and each of the degenerate modes splits into three or two distinct normal modes in the crystal as the case may be. This kind of splitting may be referred to as splitting due to degradation of symmetry. The separation between the split components may not be very prominent in cases like aragonite which possesses a pseudo-hexagonal symmetry whereas it may be

quite appreciable in cases where the departure from the ideal symmetry is appreciable.

Apart from this kind of splitting we may obtain a further multiplication of lines on account of the fact that each unit cell contains more than one ion or molecule as the case may be. Every normal mode of the free ion on this score will be replaced by m normal modes in the crystal if m is the number of ions or molecules contained in the unit cell. This situation arises out of the fact that the m ions contained in the unit which are not stirctly identical with each other in the matter of their environment may all oscillate in accordance with a particular normal mode, some of them moving in phase and others out of phase and *vice versa*. We get several such possibilities but the frequencies of all these combinations will not be very different from each other as the coupling forces between various groups are not very strong. This kind of splitting, the origin of which may be traced to the environmental changes from one ion to another in the same unit cell of a crystal, will be much less prominent than the splitting due to degradation of symmetry and will be of the same order as the shifts that are usually obtained with changing concentrations in certain Raman frequencies due to ions in solution.

The third direction in which changes may occur as we pass from a free ion to a crystal is in respect of the selection rules. Very often, at least one component arising from a given Raman active mode of the free ion will be Raman active in the crystal and conversely, every Raman active mode of the crystal would have arisen from one or other such modes of the free ion. Exceptions may occur and an example is the line at 852 appearing in the Raman spectrum of aragonite and arising from an inactive mode of the free CO_3 ion. Similarly, one of the transverse oscillations of the free Hg_2Cl_2 molecule which is Raman active becomes inactive in the crystal and another which is inactive in the molecule becomes Raman active in the crystal.

From what has been stated in the foregoing, it is clear that the Raman spectrum of a crystal need not be identical with that obtained either in the molten or dissolved states of the same substance but may differ in one or all of the following respects. Some of the lines may split into close components, additional lines may appear, and some of the lines may disappear in the crystal. It may nevertheless be noted that the splitting is usually very small and that the latter phenomena are of infrequent occurrence, and this explains the general similarity that has frequently been noticed in the literature between the Raman spectra of crystals and the corresponding solutions.

We will now consider the lattice oscillations. As has already been mentioned, the pure rotations and translations of the free ions suitably

combine with each other to give the lattice oscillations of a crystal. These may accordingly be divided into two classes, namely, the rotational type and the translational type. The two Raman active lattice oscillations (see Q'_{15a} and Q'_{17a} of Fig. 3*b*). in calcite coming under the class E_2 are nice illustrations of both these two types. Q'_{15a} is a combination of the rotation of one CO_3 group about the Y-axis with a similar rotation of the other CO_3 group. Q'_{17a} is on the other hand obviously one of the translational type. This result promises to be of great significance in connection with the controversy[19] regarding the origin of the low frequency Raman bands obtained in certain organic solids such as solidified benzene and carbon disulphide. In the light of the results that have been presented in the foregoing pages, much of the controversy in this respect appears to be merely a matter of naming the observed phenomenon. It is obvious that all organic crystals are likely to exhibit lattice oscillations in Raman effect some of which will be of a rotational type and some of a translational type and therefore the occurrence of such lines in solids need not be the occasion for postulating any special mechanism. As the temperature increases the amplitude of the motion increases and the rotational lattice oscillations will gradually pass over into free rotations either in the liquid state or even at temperatures higher than the boiling point. If the liquid state consists of quasi-crystalline groups, it is clear that these incomplete rotations will persist and will give Raman bands which are spread out just at the places where the solid gives the lattice lines. It may also be observed that if a lattice oscillation of the rotational type is permitted to appear in Raman effect, its intensity will be very closely connected with the optical anisotropy of the ion. A detailed correlation of the observed low frequency Raman bands in cases like solid benzene with their known crystal structures is however very desirable and will be taken up by us in a separate communication.

XIII. Summary

A theory of the normal oscillations of crystal lattices is presented. The selection rules in respect of Raman effect for various types of normal oscillations are considered in detail. The method of obtaining the normal co-ordinates is indicated.

The normal modes of oscillations of some typical crystal lattices are worked out with the help of this theory. They have been classified as translational, lattice and internal oscillations and the selection rules appropriate to Raman effect and infra-red absorption are given in each case. The

[19] See papers by S. C. Sirkar and others in the *Indian Journal of Physics* and by C. S. Venkateswaran in the *Proceedings of the Indian Academy of Sciences*.

manner in which the normal modes of free ions and molecules combine or modify to give the modes of the corresponding crystals is discussed in detail. The available experimental results are compared with the theoretical conclusions. In view of its importance, the case of calcite is dealt with at some length both in regard to its normal modes and the directional excitation of Raman effect.

Amongst the general results that have been obtained, mention may be made of the following. When a group of atoms constituting an ion or a molecule goes to build up a crystal, its normal modes usually undergo three types of modifications, namely, splitting of degenerate vibrations, multiplicity due to the unit cell containing more than one molecule and alterations in selection rules. Accordingly some of the Raman lines that appear in the liquids or solutions may split into components in the corresponding crystals or may fail to appear or may appear along with some new Raman lines. The lattice oscillations are divided into two types, namely, translational and rotational. It is observed that the low frequency Raman bands recorded in solid organic substances are of this type and that no special mechanism need be postulated for explaining their presence.

SYNTHETIC EXPERIMENTS IN THE BENZO-PYRONE SERIES

Part I. Synthesis of Karanjin-α-Carboxylic Acid

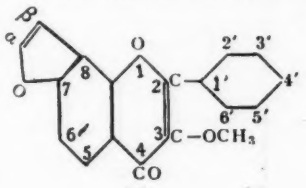
By S. Rangaswami and T. R. Seshadri

(From the Department of Chemistry, Andhra University, Waltair)

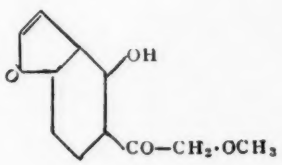
Received February 23, 1939

Karanjin was first isolated in a crystalline condition from the oil of *Pongamia glabra* by Limaye in 1922. It was subsequently obtained by Beal and Katti[1] from the same source. The constitution of this compound has been under investigation by Limaye for a fairly long period. His results have been reported mostly in the form of abstracts[2] and details of his experiments are not fully available. Through the kindness of this author we have been able to get a copy of the report of the Ranade Industrial and Economic Institute, Poona, for 1924 wherein some of his early experiments are described. The substance was found to melt at 158° and to have the composition $C_{18}H_{12}O_4$. Demethylation using hydrobromic acid gave rise to a good yield of a hydroxy-compound called karanjonol ($C_{17}H_{10}O_4$) melting at 192–93°. The acetyl derivative of this compound melted at 175–76°, the benzoyl derivative at 180° and the ethyl ether at 125–26°. The reactions of karanjin as well as those of karanjonol indicated that they belong to the flavone group of compounds.

By the decomposition of karanjin with potash Limaye[2] isolated four products :—(1) a hydroxyketone having the formula $C_{11}H_{10}O_4$ (II), (2) karanjic acid, $C_9H_6O_4$ (III), (3) karanjol, $C_8H_6O_2$ (IV) and (4) benzoic acid. Karanjol could be obtained by the decomposition of karanjic acid and could be easily converted into the acid by boiling aqueous sodium bicarbonate. It was considered to be 4-hydroxy-coumarone and this idea was confirmed by synthesis. The constitution of karanjin was therefore represented as that of 3-methoxy-flavono-7 : 8-furan (I)



(I)



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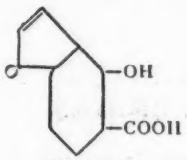

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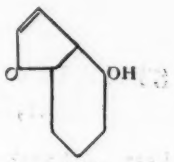
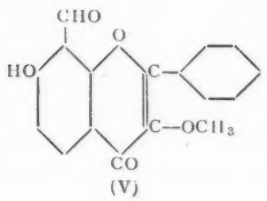


(IV)

Recently Manjunath *et al*[3] have published in detail the reactions and decomposition products of karanjin. They have placed the above constitution beyond doubt by degrading karanjic acid into well-known products. They obtained the hydroxy-ketone (II) as the main product of the action of alcoholic potash on karanjin and they were able to convert the ketone into the original karanjin by the method of Allan and Robinson thereby definitely proving that karanjin is a flavone.

Having prepared the aldehydes of 7-hydroxy-chromones and flavones[4] we have been engaged for some time on the conversion of these into chromono- and flavono-furans. Since Limaye had indicated his proposed route to the synthesis of karanjin through karanjol[2] we intended to obtain it by a different way from 3-methoxy-7-hydroxy-flavone-8-aldehyde (V). Though we have not been completely successful in our efforts, in view of the announcement of Manjunath *et al* that they are making attempts to effect a complete synthesis of karanjin we have to record in this paper the results of our experiments leading to the synthesis of 3-methoxy-flavono-7 : 8-furan-α-carboxylic acid (VIII) which can be called karanjin-α-carboxylic acid.



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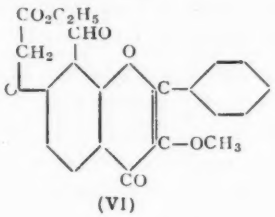

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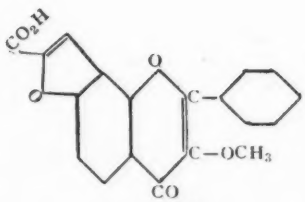
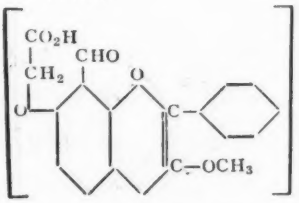


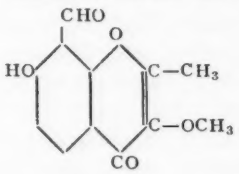
(VIII)



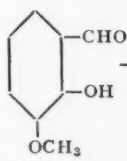
(VII)

As the first stage in our synthesis of karanjin the hydroxy-flavone-aldehyde (V) had to be condensed with a halogeno-acetic ester to yield the carbethoxymethyl ether (VI). The methods adopted by Späth and Pailer[5] and Limaye *et al*[6] in analogous cases of coumarin compounds were examined. They heated a mixture of the sodium derivative of the hydroxy-compound with iodo-acetic ester or bromo-acetic ester and obtained good yields of the condensation product. Though this was successful when we employed 2-methyl-3-methoxy-7-hydroxychromone-aldehyde (IX) it failed in the case of the corresponding flavone compound. After examining different methods it was discovered that by simply heating a mixture of the hydroxy-aldehyde and bromoacetic ester in benzene solution in the presence of potassium carbonate the condensation went remarkably well and gave rise to a good yield (70%) of the product (VI). It was noted that in the case of simpler aldehydes this treatment though successful did not give rise to such a good yield.

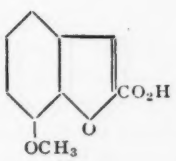
For the hydrolysis of the ester hot alcoholic potash that had been employed in analogous cases was not successful. There was considerable decomposition resulting in very poor yields. The most satisfactory method was to employ aqueous potash and to boil the mixture till solution was effected. But the interesting part of the hydrolysis was that it was accompanied by ring-closure giving rise to 3-methoxyflavono-7 : 8-furan-α-carboxylic acid (VIII) instead of the expected aldehydo-acid (VII). The above-mentioned workers on the coumarin series obtained simple hydrolysis by means of alcoholic potash and there was no ring-closure which had to be subsequently effected by heating with acetic anhydride and sodium acetate. The experiments of Reichstein *et al*[7] who obtained 7-methoxy-coumarone-2-carboxylic acid (XI) by boiling *ortho*-vanillin (X) with bromoacetic ester in the presence of sodium ethoxide show that there exists the possibility of the furan ring-closure under these conditions. That the furan-carboxylic acid is obtained by the hydrolysis of the aldehydo-ester is not only supported by the analytical data but is further confirmed by a study of the absorption spectra of karanjin (I), of the carboxylic acid (VIII) and of the carbethoxy-methyl ether (VI). The first two resembled each other very closely and differed markedly from the last.



(IX)



(X)



(XI)

The final stage in the synthesis, *i.e.*, the decarboxylation of the acid (VIII) has been found to be difficult. It is quite stable under conditions which have been ordinarily found useful to remove the carboxyl group. On strong heating it undergoes a complex change giving rise to products which do not melt. Further attempts to effect this decarboxylation are in progress.

Experimental

The sodium salt of 2-methyl-3-methoxy-7-hydroxy-chromone-8-aldehyde (IX).—The hydroxy-aldehyde was dissolved in the least possible quantity of hot anhydrous methyl alcohol and the hot solution treated with the calculated quantity (1 mol.) of sodium methoxide in alcohol. A solid began to separate in the course of a few minutes. The mixture was cooled and treated with excess of anhydrous ether to precipitate all the sodium salt which was then filtered with suction, washed with ether and dried in a vacuum desiccator.

Carbethoxymethyl ether of 2-methyl-3-methoxy-7-hydroxychromone-8-aldehyde (IX).—The sodium salt (0·4 g.) was heated with ethyl bromoacetate (3–4 c.c.) for 8 hours in an oil-bath at 170–75°, the liquid being kept gently boiling. Excess of the ester was then removed by distillation under reduced pressure. The solid residue was treated with water, left exposed to the open air for a day to get rid of the last traces of the bromoacetic ester and then filtered and washed. It was subsequently stirred with cold dilute alkali and washed again with water. The resulting solid was a pale yellow powder which was quite crystalline and melted sharply at 180° (m.p. of the parent compound 180°, mixed m.p. 150–52°). When recrystallised from alcohol the carbethoxymethyl ether came out as very thin rectangular and rhombic plates, the melting point being the same as before. (Found : C, 60·2; H, 5·3; $C_{16}H_{16}O_7$ requires C, 60·0, H, 5·0%.) The compound gave no colour with alcoholic ferric chloride (the original hydroxy-aldehyde gave a blood-red colour). Yield—80%.

Carbethoxymethyl ether (VI) of 3-methoxy-7-hydroxy-flavone-8-aldehyde (V).—The hydroxy-flavone-aldehyde (0·5 g.) was dissolved in a slight excess of hot benzene (40 c.c.) that had been dried over calcium chloride and treated with ethyl bromoacetate (4 c.c.) and freshly ignited potassium carbonate (2 g.). The mixture was kept gently boiling under reflux for 16 hours in a water-bath. The clear hot benzene solution was then carefully decanted into a crystallising dish and left exposed to a current of air for slow evaporation. The solvent and excess of bromoacetic ester were lost in a few hours and a colourless crystalline solid (flakes) remained behind. This when washed with a little ether to remove the last traces of bromoacetic ester melted at 115–16° and was sufficiently pure for further hydrolysis. For analysis the sample

was crystallised from methyl alcohol from which it separated as prismatic needles melting at 116–17°. (Found : C, 66·1 ; H, 4·7 ; $C_{21}H_{18}O_7$ requires C, 66·0 ; H, 4·7 %). Yield—0·4 g.

The compound was highly soluble in methyl and ethyl alcohols and insoluble in cold dilute alkali and it gave no colouration with alcoholic ferric chloride. It melted smoothly during combustion but decomposed slowly when strongly heated and the decomposition product could only be burnt very slowly.

Hydrolysis to 3-methoxyflavono-7 : 8-furan-α-carboxylic acid (VIII).—When the foregoing ethyl ester (1 g.) was heated with 5% aqueous potash (50 c.c.) on a wire-gauze most of it went into solution before the boiling point was reached and the little solid that remained was also got into solution by boiling for about a minute. The hot solution which was orange in colour was set aside for half an hour, after which it was cooled under the tap and shaken with ether to remove any non-acid impurities. The lower alkaline layer was filtered through a fluted filter paper and the clear filtrate acidified with hydrochloric acid. A pale yellow fluffy solid separated slowly when the acidic mixture was left in the ice-chest for half an hour. This was filtered and washed with water.

The above crude acid on being ground in a mortar with cold saturated sodium carbonate solution was mostly transformed into a crystalline yellow solid (the sodium salt). This was filtered from the orange-red solution. The filtrate gave on acidification a very small quantity of a coloured solid which was discarded. The residue on the filter paper when washed with water first became colourless and then readily dissolved to give an almost colourless solution. When this was acidified with a few drops of acid it gave a perfectly colourless precipitate which after filtration and washing with water was crystallised from alcohol. The flavono-furan-α-carboxylic acid was thus obtained as narrow rectangular plates melting at 224–26°. (Found : C, 68·2 ; H, 4·0 ; $C_{19}H_{12}O_6$ requires C, 67·9 ; H, 3·6%). Yield—20%.

The acid was sparingly soluble in water from which it separated in the form of needles and moderately soluble in alcohol. With 2N sodium hydroxide and concentrated sodium carbonate solutions most of the acid separated out as the sparingly soluble sodium salt. This behaviour is very common with benzofuran-carboxylic acids. The acid had a marked tendency to sublime unchanged giving rise to shining needles.

Summary

2-Methyl-3-methoxy-7-hydroxychromone-8-aldehyde formed a sodium derivative which readily condensed with bromoacetic ester to form the

corresponding carbethoxy-methyl ether. This reaction did not take place satisfactorily with 3-methoxy-7-hydroxyflavone-aldehyde. The condensation was, however, smoothly effected in boiling benzene solution in the presence of potassium carbonate. When hydrolysed with aqueous potassium hydroxide, simultaneous ring-closure took place to yield 3-methoxyflavono-7 : 8-furan-α-carboxylic acid which is considered to be karanjin-α-carboxylic acid.

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THE CAUSE OF COLOUR OF THE BLUE QUARTZES OF THE CHARNOCKITES OF SOUTH INDIA AND OF THE CHAMPION GNEISS AND OTHER RELATED ROCKS OF MYSORE

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Introduction

The nature of mineral colours has been a subject of much study especially during the last few decades. Investigations of the cause of colour of minerals, and its variation with physical and chemical properties as well as with temperature, were carried out systematically only in recent years. Such investigations were carried out mainly with the common coloured quartzes like smoky quartz, amethyst and rose quartz, and some other coloured minerals, prominent among which are zircon, topaz, tourmaline, fluorite, emerald, ruby, etc. But the charnockite blue quartz, which is as abundant as any of the other coloured quartzes, has not received much attention from mineralogists or physicists so far.

Holland[1] investigated the greyish-blue charnockite quartz from South India and observed the presence of acicular inclusions which he considered to be rutile. He reported that the colour of the quartz was probably due to those inclusions, but he does not appear to have either isolated the inclusions or carried out a chemical investigation of the quartz specimens.

The blue quartzes of Nelson and Co., Virginia, which were investigated by Dunnington[2] and Robertson[3] possess a colour which is unaffected by heat but showing at the same time some relation to their TiO_2 and Fe_2O_3 contents, while those of Pfaffenreuth show a very unstable blue colour which according to Weinschenk[4] is due to the manganese and iron content of these quartzes. The colour of these quartzes, which is of an yellowish-red tone by transmitted light and blue by reflected light, disappears even on gentle heating. The colour is found to be unstable even in direct sunlight. Further, the Pfaffenreuth quartz is found to contain inclusions of needles with high birefringence and weakly birefringent droplets. Finally Weinschenk

comes to the conclusion that there is a possibility of dilute dyes playing a rôle in the colouring of this quartz. The cause of the blue colour in the quartz from Rumberg in Bohemia, described by Von Cotta[5] could not be determined microscopically. Robertson[6] and Iddings[7] hold the view that the colour of blue quartz is due only to the microscopic acicular inclusions of rutile, and Postelmann[8] also comes to the same conclusion. Watson and Beard[9] observe that the blue quartz of the Virginia rutile area owes its colour to the presence of acicular inclusions of rutile, the phenomenon being attributed to the behaviour of light reflected from the surface of these inclusions.

The present paper describes the results obtained by chemical and microscopic examination of the specimens and the light they throw on the problem of colouration of minerals.

Physical and Chemical Properties.—

Specimens of charnockite quartz with varying intensity of blue colour as well as the opalescent blue quartz from the champion gneiss and related rocks of Mysore were examined in the course of this work. The colour of these quartzes which is of an yellowish tone by transmitted light and blue by reflected light was found to be greatly affected by heating, the charnockite quartz losing its colour completely even at 300° C.

The charnockite quartz occurs as crystal aggregates in the acid charnockites. The crystal mass shows considerable cracking and granulation. The colour of this quartz is not very dark, but it is definitely blue with a greyish tint.

Boiling with hydrochloric acid was found to free the crushed specimens totally from the iron present as an impurity, but since the blue colour of the specimen persisted even after this treatment, it appears that iron compounds do not contribute to the colour of the specimen.

Specific gravities of the various quartzes :

(i) Pallavaram charnockite blue quartz (*B*) " Type Specimen "	2·660
(ii) Pallavaram charnockite colourless quartz (*F*) ..	2·665
(iii) Pallavaram charnockite blue quartz (*A*)	2·662
(iv) Colourless glassy quartz from Nellore	2·661

Microscopic examination of the blue quartz specimens with varying intensities of colour.—

The Charnockite quartz specimens—(A) Specimens coloured more intensely than others.—These were collected from the Pallavaram Hill and are few

in number. In their microscopic properties they are similar to (*B*), described below, excepting for the intensity of the colour of the turbid medium which is more prominent than in (*B*). The distribution and arrangement of the various inclusions are exactly the same as in (*B*).

(*B*) *The common charnockite blue quartz.*—"*Type Specimen*"—This was collected from the so-called "Charnockite-pegmatite" of Holland, a coarse grained rock composed mainly of blue quartz and microperthitic microcline occurring as contemporaneous or segregation veins in the type mass of charnockite which forms a low hill on the western side of the St. Thomas Mount.

When a thin section of this quartz is examined under the microscope it shows an enormous number of inclusions which can be classified under two heads, *viz.*, (*a*) *regularly arranged* acicular inclusions (Microphotographs 1, 2) and (*b*) *the more or less irregular drop-like and dust-like inclusions showing much variation in size* (Microphotographs 3, 4). When sections cut perpendicular to the *C*-axis are examined between crossed nicols the acicular inclusions are highly birefringent while the others are almost isotropic, a few of them, however, being weakly birefringent. The quartz grains which appear to be homogeneous shapeless crystals are found, when examined under the microscope between crossed nicols, to be made up of many crystal grains in different orientations. Thus, this definitely shows that the quartz has undergone fragmentation at some stage or other. Further, most of the individual grains show strain shadows. Often, the acicular inclusions extend through adjacent fragments of the quartz in unbroken continuity indicating thereby either a secondary origin for these acicular inclusions or a secondary arrangement not along cracks produced by orographic movements as suggested by Johannsen[10] due to molecular movement of titanium when the magma was in a plastic condition.

A thin section of this quartz shows between parallel nicols a pale brownish-yellow turbidity which is not so prominent as in the Mysore blue quartz A. 762 described below. The presence of this coloured turbid medium can be easily detected even in fairly thick sections under low power. The dust-like and drop-like inclusions are found either scattered uniformly throughout the quartz or congregated in patches or lines like strings of pearls (Microphotographs 5, 6).

The arrangement of the acicular inclusions in two different sections of the quartz is as follows :

In sections parallel to the prism (110).—

NEEDLE GROUPS	REMARKS
(1) Parallel to the axis of minimum optical elasticity, *i.e.*, parallel to the *C* or vertical axis.	One set of needles of equal length lying almost in the plane of the section. 50 to 100 μ in length.
(2) Parallel to the fast direction, *i.e.*, parallel to one of the lateral crystallographic axes and exactly at right angles to system (1).	One set of needles lying in the plane of the section. Average length is about 100 μ. Needles varying in length from 200 to 300 μ are also met with.
(3) Parallel to a direction which makes an angle of 38° with system (2) and 52° with system (1).	One set of needles of almost equal length lying in the plane of the section. Length 50 to 100 μ.
(4) Parallel to a direction which makes an angle of 38° with system (1) and 52° with (2).	One set of needles similar to system (3) but lying not exactly in the plane of the section.
(5) Parallel to a direction which makes an angle of 15° with system (2) and 75° with system (1).	Only a few needles—not exactly in the plane of the section. Needles are comparatively short—25 to 50 μ in length.
(6) Parallel to a direction which makes an angle of 30° with system (2) and 60° with (1).	Needles fairly long but not in the plane of the section. They are also few in number. Length 100 to 200 μ.
(7) Parallel to a direction which makes an angle of 30° with system (1) and 60° with (2).	Similar to system (6). Length 100 to 200 μ.
(8) Parallel to a direction which makes an angle of 15° with system (1) and 75° with system (2).	Similar to system (5). Do not lie in the plane of the section. Length 10 to 50 μ.
(9) Parallel to a direction which makes an angle of 5 to 10° with system (1).	Very short needles—not in the plane of the section. Length 10 to 25 μ.
(10) Parallel to a direction which makes an angle of about 5° with system (2).	Similar to system (9). Length 10 to 25 μ.

The section was also studied under dark-field-illumination to search for needles perpendicular to the section examined. The cut ends of needles were then found to stand out as bright points of light showing the presence of needles perpendicular to the section, that is, needles lying in a direction parallel to the secondary planes of symmetry of quartz crystal.

In a section perpendicular to the C-axis.—

Here the sets of needles are less in number and they are easily made out. Their characters can be studied without much difficulty owing to the isotropic nature of the section which is cut perpendicular to the optic axis of the crystal. There are seven well-defined sets of needles which can be easily recognised in thin sections and they are as follows :

(1), (2), (3).—These three sets of needles are almost of equal length (about 100 μ) crossing one another at an angle of 60°. All these needles lie in the plane of the section.

(4), (5), (6).—These three sets are almost similar to sets (1), (2) and (3) but they exactly bisect the angle (60°) formed by the latter sets. They cross one another at an angle of 60°. Average length is about 75 μ.

(7) There is one set of needles lying almost parallel to one of the three above-mentioned sets, but not lying in the plane of the section. These needles vary in length from 100 to 150 μ.

There are also two or three other sets of very short needles (5 to 10 μ) not lying in the plane of the section. These sets comprise only very few needles.

The above observations regarding the arrangement of the needles in the two sections can be summarised and classified as follows :

(*a*) There is one set of needles parallel to the vertical or *C*-axis.

(*b*) There are three sets of needles parallel to the three lateral crystallographic axes of the quartz and thus lie in the principal planes of symmetry.

(*c*) There are three sets of needles lying parallel to directions which bisect the angles formed by the lateral crystallographic axes, that is, they lie in the secondary planes of symmetry.

(*d*) There are two sets of needles parallel to the faces of the unit rhombohedron.

(*e*) There are six other sets of needles in a section cut parallel to the prism and about three in a section cut perpendicular to the *C*-axis which do not lie in the plane of the section and therefore could not be identified with any of the crystallographic directions.

While referring to the set of needles which is supposed to be parallel to the face of the unit rhombohedron, Holland[1] remarks that this set meets the vertical axis at an angle of 52° instead of at 38° and the trace of the basal plane at an angle of 38° instead of at 52°. As found out by Holland the needles lying in the basal sections of the quartz show straight extinction and are highly birefringent.

(*C*) *A blue quartz from Pallavaram Charnockite less intense in colour than* (*B*).—The acicular and dust-like and drop-like inclusions are as abundant as in (*B*). The brownish-yellow turbidity is slightly less intense and the arrangement and distribution of the inclusions are exactly the same as in (*B*).

(*D*) *A blue quartz from Pallavaram Charnockite less intense in colour than* (*C*).—The abundance and distribution of the inclusions are similar to both (*B*) and (*C*) excepting for the faintness of the brownish-yellow turbid medium.

(*E*) *A very faintly coloured blue quartz from the Pallavaram Charnockite.*—The abundance and distribution of the inclusions are almost similar to *B*, *C* and *D*. The brownish-yellow turbidity is almost absent in thin sections and is very faint in thick sections.

(*F*) *A colourless quartz from the Pallavaram Charnockite area.*—This specimen contained the acicular inclusions described above but was almost free from the innumerable specks of dust-like material and weakly anisotropic droplets present in the blue varieties. The acicular inclusions were as abundant as in some of the blue varieties, but the brownish-yellow turbidity was not noticeable. Like the blue variety this quartz also shows fragmentation and strain shadows. The grains of this quartz show extensive longitudinal cracking, almost parallel to the vertical crystallographic axis but the cracks are too widely spaced to mask any colour effect. Even individual grains which exhibit no cracking are found to be colourless, whereas in the blue varieties, the colour persists even in the highly cracked portions.

(*G*) *A colourless quartz from Bodi Charnockite, Madura* (*from Karattu Petti Hill*).—When examined under the microscope, this specimen was found to be almost free from the acicular inclusions, but the dust-like and drop-like inclusions were present as in the blue varieties. Further, no brownish-yellow turbidity was noticed nor any signs of fragmentation or wavy extinction. This specimen also is traversed by longitudinal cracks which run more or less parallel to the vertical crystallographic axis. Here also, as in (*F*), the cracks are fairly widely spaced.

(*H*) *An ignited sample of blue quartz* (*B*).—The specimen (*B*) was heated for 13 hours at 300°, when it was found that it had lost its colour. Examination under the microscope revealed that the turbidity originally present was no longer noticeable, but in other respects the specimen appeared to have retained all its characteristics.

A. 762. *A quartz-porphyry from Kadur District* (*Mysore*).—This rock shows the presence of both blue as well as almost colourless quartz grains. When a thin section of the rock is examined in transmitted light the blue quartz grain is found to be coloured by an almost uniform brownish-yellow tint which is absent in the colourless grains. The intensity of this brownish-yellow colour is found to be directly proportional to the intenisty of the blue colour of the quartz when it is seen in reflected light. This colour, like the blue colour, is destroyed by heat. Like the charnockite quartz this quartz also shows the presence of acicular inclusions. The microscopic dust-like and drop-like inclusions are also found in abundance.

Very fine acicular inclusions are found crowded in the regions coloured brownish yellow showing, as it is now definitely known that these inclusions are rutile needles, that those regions are rich in titanium. The yellow colouration is mostly produced, judging from the chemical analyses given below, by a titanium compound and not by the acicular inclusions owing to the dispersed nature of the colour film in the areas between needles. Further, *there are also found some grains of quartz which show the strong brownish-yellow tint in transmitted light and blue in reflected light and yet are completely free from inclusions of any type even when observed under oil-immersion magnification.*

The acicular inclusions are not so prominent in size as in the charnockite blue quartz, but they are definitely more in number and more closely packed. The colour of this quartz is more prominent than the charnockite quartz and the turbid medium is also denser than in the charnockite quartz. In most of the colourless quartz grains of the same rock section both the acicular inclusions and the brownish-yellow colouration are absent. But there are present in such grains very small yellow coloured patches in which a few needles of rutile are present congregated. There are also present a few colourless quartz grains showing the presence of acicular inclusions which are as densely packed as in the coloured grains and at the same time are devoid of the brownish-yellow turbidity.

The acicular inclusions in this quartz are, in general, extremely fine and a very high magnification is required even to observe them. These inclusions unlike those of the charnockite quartz, are not arranged with crystallographic regularity within the body of their host. The dust-like

and drop-like inclusions are as abundant in the colourless grains as in the coloured ones and their arrangement is also similar to those present in the coloured ones. As in the charnockite quartz, these dust-like and drop-like inclusions appear to be strained acidic glassy matter. Some of them also appear to consist of opaque iron compounds. As the powdered specimen suffers some loss of weight on ignition some of the drop-like inclusions are perhaps liquid inclusions in cavities.

Z 4/539. *An opalescent blue quartz of Champion Gneiss from the E.S.E. spur of the* 3803 *near S.U.N. Se, Mudgere Taluk (Kadur District, Mysore).*—Unlike A.762 a thin section of this quartz shows zoning parallel to the outer margin of the crystal. The colour of this quartz suffers considerable paling when heated, but is not completely destroyed even on heating to nearly 1000° C. The brownish-yellow to grey turbid medium is very dense along definite parts of the crystal forming as it were bands which give rise to the zoning effect. The acicular inclusions are very crowded towards the bands leaving the interspaces between the bands almost free or only with a few scattered needles. The interspaces between the bands are also faintly coloured by the brownish-yellow turbid medium which, however, is slight.

A comparison of this blue quartz with A. 762 reveals some interesting points. The blue colour of A. 762 is more intense than that of this quartz. The acicular inclusions in A. 762 observed under microscope are found to be smaller in size and less prominent than Z4/539. In A. 762 the brownish-yellow turbid medium is more intense than in Z4/539. In Z4/539, the microscopic dust-like and drop-like inclusions are as abundant as in A. 762. In Z4/539, the colour of the turbid medium is slightly modified by a greyish-tint, perhaps due to the predominance of the inclusions of rutile needles. Perhaps, this is also responsible for the greyish tint observed in this quartz and also in the charnockite quartz specimens when they are examined in reflected light.

A number of sections of champion gneiss and other rocks with opalescent blue quartz from the Mysore Geological Survey Department, kindly lent by the Director of the Department, were studied by me and the results are given below :—

J5/65. *Champion Gneiss. K.G.F.*—The quartz grains exhibit the unmistakable opalescent blue colouring in reflected light. The rock as a whole looks highly granulated and the quartz occurs as large patches which between crossed nicols show innumerable grains of quartz having different orientation. Both the acicular inclusions and the dust-like and drop-like inclusions are present. The brownish-yellow turbidity is not very prominent. The

acicular inclusions of rutile are not present as abundantly as the charnockite or A. 762 or Z4/539.

Number of needles per c.c. of quartz ..	350,000
Average length of the needles	40 μ
Thickness	about 0·5 μ

M_1/349. *Champion Gneiss* (?) *from Holenarsipur.*—The quartz grains in this rock exhibit the characteristic opalescent blue colour. The brownish-yellow turbidity in this quartz is easily perceptible. *The quartz grains are completely free from acicular inclusions but they contain the dust-like and drop-like inclusions.*

H_{11}/946. *Champion Gneiss, Shimoga District.*—This is a fine grained specimen with porphyritic blue opalescent quartz. The quartz grains show clearly the presence of the brownish-yellow turbid medium. *Excepting for a very few scattered needles of rutile the acicular inclusions are completely absent.* It is noteworthy that this quartz which shows such intense blue colour is almost completely free from acicular inclusions. The dust-like and drop-like inclusions are present.

The quartz loses its colour on heating but does not show the development of cracks. The milky blue colour of the quartz in reflected light is very prominent.

M_1/560. *Basic Xenolith in Banavar Granite.*—The quartz grains in this rock show a striking resemblance to the charnockite quartz. They are almost rounded in shape. The abundance and distribution of dust-like and drop-like and the acicular inclusions are almost similar to the charnockite quartz excepting that the acicular inclusions are smaller in size. Like the charnockite quartz the brownish-yellow turbidity is rather faint and the colour in reflected light is an opalescent greyish blue.

Number of acicular inclusions per c.c. of quartz ..	= 455,000
Average length of needles	= 40 μ
Thickness	= 0·5 μ

M_2/233. *Chitaldrug Granite.*—Quartz occupies sufficiently large areas. *It is almost free from acicular inclusions,* but contains the drop-like and dust-like inclusions to the same extent as most of the charnockite quartzes. The quartz has suffered the same amount of granulation as the charnockite quartz. The dispersed brownish-yellow turbid medium is clearly seen and the milky blue opalescent colour could be easily detected.

Chemical analysis of the impurities present in the various specimens of quartz.—

Method of procedure.—The impurities in the blue quartz were analysed before and after washing the roughly powdered material with hot concentrated

hydrochloric acid and finally with water. The faint blue colour which is also visible in the roughly ground wet material is not lost by this treatment showing thereby that the colour of this quartz is not affected by this acid treatment. This further shows that the impurities detected in the acid-treated samples alone should be responsible for the colouration of this quartz. Loss of weight on ignition was determined in all cases but it showed no relation to the depth of colour of these quartzes.

Estimation of Iron and Titanium.—Iron and titanium were determined colorimetrically as follows: The dried and weighed quartz powder from the hydrochloric acid treatment was fused with potassium bisulphate and the melt after cooling was taken in dilute hot H_2SO_4 and the silica was removed by filtration. The iron and titanium were then independently determined colorimetrically in the filtrate using potassium thiocyanate as reagent for iron and hydrogen peroxide for titanium.

For the estimation of other constituents about five to ten grams of material were taken and fused with Na_2CO_3. The cooled melt was dissolved in dilute HCl and the silica was removed completely by two evaporations. The third group metals (Fe, Al, Ti) were removed by filtration after precipitating them with ammonia and ammonium chloride. Calcium and magnesium were determined in the filtrate. Calcium was precipitated as oxalate and the precipitate was ignited and weighed as oxide. Magnesium was determined as usual as pyrophosphate.

To find out the real nature of the impurities present in the quartz (*B*) the quartz was chemically analysed before and after washing it with hot concentrated hydrochloric acid.

Results of analysis

TABLE I

The composition of the impurities in the blue quartz B

Oxides	Before washing with HCl	After washing with HCl
	per cent.	per cent.
Fe_2O_3 ..	0·150	0·008
TiO_2 ..	0·024	0·024
CaO ..	0·120	nil
MgO ..	trace	nil
Total ..	0·294	0·032

TABLE II

Ti and Fe content of various specimens of quartz and the loss of weight suffered by them on ignition

	Quartz	TiO_2 %	Fe %	Loss on ignition %
(i)	The blue quartz from Mysore (A. 762) (The average composition of the coloured and the colourless grains)	0·030	0·005	..
(ii)	The Pallavaram (charnockite) blue quartz (A)	0·030	0·011	0·18
(iii)	Do. do. (B)	0·024	0·006	0·11
(iv)	Do. do. (C)	0·020	0·005	0·12
(v)	Do. do. (D)	0·018	0·004	0·15
(vi)	Do. do. (E)	0·014	0·004	0·19
(vii)	Colourless quartz from Pallavaram (charnockite) (F) ..	0·002	0·001	0·11
(viii)	Colourless quartz from Bodi (charnokite) (G)	..	0·002	..
(ix)	Z4/539 Opalescent blue quartz from Champion gneiss ..	0·025	0·010	..
(x)	J5/65 Blue quartz of Champion gneiss from K.G.F. ..	0·024	0·012	..
(xi)	H 11/946 Blue quartz from Champion gnesis from Shimoga District	0·028	0·005	..
(xii)	M_1/349 Blue quartz from Holenarsipur	0·017	0·015	..
(xiii)	M_2/233 Blue quartz from Chitaldrug granite	0·025	0·005	..
(xiv)	M_1/560 Blue quartz from the basic xenolith in Banavar granite	0·024	0·004	..

Samples (i) and (ix) to (xiv) were kindly lent by the Department of Geology, Mysore.

Postelmann has devised an easy method for separating from the quartz the needles of rutile present therein. The method consists in dissolving out all the quartz from the roughly crushed specimen in hydrofluoric acid at ordinary temperature. To find out whether in the charnockite quartz also these inclusions are rutile the following procedure was adopted :

About 15 to 20 grams of the roughly crushed quartz was treated with about 25 c.c. of 40% hydrofluoric acid in a platinum dish at the room temperature for about 60 hours. Finally the excess of hydrofluoric acid was poured out by careful decantation and 50 c.c. of water was added to the residue which contained about 5 grams of undissolved quartz and a dark slimy deposit. Then the water was stirred till it was somewhat turbid and this turbid solution was allowed to settle for 8 hours and then carefully poured out by decantation so that the sediment at the bottom was not disturbed.

This process of washing was repeated twice again so that most of the acid was removed. Finally about 25 c.c. of water was added to the residue and stirred well. 5 c.c. of concentrated hydrochloric acid was then added and the dish heated for 4 hours on a water-bath and then allowed to settle for 4 hours. The original process of washing was again repeated to remove the excess of hydrochloric acid. The residue which was thus freed from iron was then washed thrice with cold water and finally stirred vigorously in about 20 c.c. of cold water. This liquid was at once poured into small evaporating dishes and evaporated to dryness over a water-bath. The dried residue was then mounted on a glass slide with canada balsam and examined under a microscope in the dark-field with oblique illumination (Microphotograph 7). The slide shows numerous perfectly detached needles scattered throughout the field. From their general character it was easily ascertained that they were rutile needles. The dried residue was also found to contain titanium.

Discussion

A careful count of the needles in the thin section of the charnockite quartz (B) showed that there were only about 405,000 needles of rutile per cubic centimetre of the quartz, the average length of the needles being about 100 μ. By assuming that all the titanium shown by the chemical analysis is present as rutile, the thickness of these needles could be calculated, and it is found to be almost 2 μ. But when the thin section of the quartz is examined under very high magnification (oil-immersion) most of the needles appear to be about 1 μ in thickness. This shows definitely that there is some titanium present other than as rutile and this is not accounted for. This additional titanium is far in excess of the titanium content of the acicular inclusions and this is also illustrated by the following example. The colourless quartz from Pallavaram, which contains about 450,000 needles of rutile per cubic centimetre of quartz with an average needle length of 60 μ, shows a titanium content of 0·002% (TiO_2). If all this TiO_2 is present as rutile, then, calculation yields a needle thickness of 0·7 μ to 0·8 μ, which is of the observed order. In the Mysore blue quartz (A. 762) which shows 0·03% of TiO_2 the number of needles per cubic centimeter of quartz is about 2,000,000 and their average length is about 30 μ. This would give a needle thickness of 1·8 μ if all the TiO_2 existed as rutile needles observed. But when the thin section is examined under oil-immersion magnification, the needles appear to be only about 0·8 μ in thickness, indicating the existence of additional TiO_2 as pointed out earlier. Dr. Postelmann's observations on the Hindenburgstein[8] reveals that the calculated thickness of needles is slightly more than 1 μ, which appears to be larger than the observed thickness.

Since the colour of these quartzes was lost on heating them, carefully prepared thin sections of these quartzes were examined under the microscope both before and after heating them with a view to ascertain whether the needles of rutile suffered any change either in the number or in their size. The results given in the following table show that the number and size of the acicular inclusions were not affected by heat and thus they do not serve to explain the loss of colour on heating.

To estimate the number and size of the rutile needles same areas in all the specimens were examined under the microscope both before and after heating. All the specimens were heated for 13 hours at a temperature of 300°.

TABLE III

Quartz	Before heating			After heating		
	Average No. of needles per c.c. of Quartz	Length	Thickness	Average No. of needles per c.c. of Quartz	Length	Thickness
A	445,500	85 μ	1–·5 μ	445,500	80 μ	1–·5 μ
B	405,000	100 μ	1–·5 μ	405,100	100 μ	1–·5 μ
C	405,000	80 μ	1–·5 μ	405,100	85 μ	1–·5 μ

The results shown in the above table indicate that the number and size of the acicular inclusions are not affected by heat. Even heating at very high temperatures has produced the same results.

While working on the " opalescent quartz gneiss " (Champion gneiss of Kadur District, Mysore) Sampat Iyengar[11] examined rocks $Z_4/539$ and $Z_4/540$ which are characterised by the presence of the bluish opalescent quartz. After a careful study of this quartz he comes to the conclusion that the pale brown colour of this blue quartz in thin sections in transmitted light is due to the presence of either rutile or amphibole prisms crossing each other at an angle of 60°. He adds further that the bluish opalescent colour of this quartz seems to be the effect of diffraction of light by such minute inclusions in the mineral. Smeeth[12] while referring to Sampat Iyengar's work remarks that the opalescent quartz grains are of a milky-blue appearance by reflected light and pale brownish-yellow in transmitted light in thin sections. He adds that in the majority of slides of rocks which he examined from localities other than those referred to by Sampat Iyengar *inclusions of this character are not noticeable and the optical effect appears to be due to microscopic dust-like inclusions.* He points out at the same time that *this is perhaps merely an*

association and the opalescent effect may really be due to an ultramicroscopic cause.

From a spectroscopic analysis of a blue corundum Islamov and Talmacev[13] have recently concluded that titanium is responsible for the production of blue colour in corundum. Though the specimens used were not examined microscopically, it supports the idea that titanium is responsible for the production of blue colour in quartz.

While working on specimens of amethyst, rose and blue quartz, Watson[9] observes that the blue quartz of the Virginia rutile area owes its colour to the presence of the acicular inclusions of rutile, the phenomenon being attributed to the behaviour of light reflected back from the surface of these inclusions. In support of this view is put forward the fact that heating does not destroy the blue colour of the quartz. This quartz however differs from those of Pfaffenreuth and those of the charnockites. Watson and Beard, in the same paper, state that in many sections of blue quartz examined by Watson the substance of this quartz was found to be crowded with hair-like inclusions of rutile, which were frequently arranged with more or less crystallographic regularity. But they also add that "*quartz of light colour or colourless to dark smoky colour often shows inclusions of rutile needles, with no indication whatever of blue colour*". Wetzel[4] while dealing with blue quartz in general, remarks that it is questionable from observed facts whether these acicular inclusions contribute to the production of dilute colours, *since in those quartzes whose colour was specially intense the number of needles was relatively small.*

The titanium content of the various quartz specimens shown in Table II presents clearly that there is a definite relationship between the TiO_2 content and the intensity of colour of these quartzes, the amount of TiO_2 increasing with the increase in the intensity of colour. In the case of the iron impurity it is not so apparent. Perhaps the trace of iron shown by these quartz specimens is merely a remnant of the unwashed original iron impurity. The amount of iron thus present is so small that it need not be taken into consideration. The loss of weight on ignition is not very striking as it is found to be more or less the same in all the specimens of quartz. Even in the colourless specimens it is of the same magnitude.

Postelmann[8] found that the iron shown by chemical analysis is only an external impurity, which coats the quartz grains and very fine fissures either brown or green, " Es tritt nur als ausserliche verunreinigung auf und stammt aus braunlichen (Nelson Co.) oder grunlichen (Cojehnen) Zarten Hautchen, die, stellenweise die Quarzkorner und deren feinste Risse uberziehen." The analyses of the charnockite blue quartz both before and after washing

with hot concentrated hydrochloric acid (Table I) also show this point clearly, namely, that most of the iron is only an external impurity and has nothing to do with the colour of the quartz. The iron is washed away by the acid and further the colour of the quartz is not affected by such washing. The trace of iron shown by the material after washing with acid is perhaps due to some residual unwashed iron left out due to incomplete washing or it might be in the body of the quartz forming the material of the dust-like inclusions. Thus it is more or less definite that titanium is the only element which is responsible for the colouration of the blue quartz.

Recently Postelmann has published a memoir on blue quartzes, but he has made no reference to the heat treatment of these quartzes. Heat treatment being an important item in the investigation of these quartzes it would be desirable to study the effect of heat on these quartzes. A colour stable to heat may mean either that it is due to some inclusions unaffected by heat or due to some stable pigment. An unstable colour may be due to various other causes. It may be due to colloidal particles of some element as proposed for the colour of smoky quartz or it may be due to an organic dye which decomposes on heating or it may be due to some inorganic compound the physical state of aggregation of which within the quartz alters on heating. If it is assumed that the colour is due to the needles alone, then the loss of colour on heating can be explained only in one way, and that is, these needls should have possessed an unstable blue colour. But it seems to be very uncertain. It cannot be argued that the quartz enclosing the rutile needles is affected by heating it even up to 400° and destroys thereby the blue colour effect produced by these needles, because the blue colour of the quartz from Nelson and Co., Virginia, is found to be unaffected by heat. Further, the charnockite quartz suffers no change on heating it up to 400° C. excepting that it loses its colour. So in those quartzes in which the colour is affeced by heat the acicular inclusions are not responsible for the production of the colour. Even in the case of the blue quartz from Nelson and Co., the author considers it possible that the colour may not be due to the rutile inclusions but due to some stable inorganic pigment.

Conclusion

A study of previous work shows clearly that no single general theory has been developed to account for the origin of mineral colours. The mode of origin of these mineral colours, as well as their constitution appear to depend upon the mode of origin and constitution of the coloured mineral and also on the impurities present in it. Doelter[14] has shown that mineral colours fall under two main categories, that is, (i) produced by colloidal and liable matter

and (ii) produced by a substance which is stable and isomorphous with the mineral. The minerals belonging to the second category offer no trouble as they are easily detected and differentiated from those of the first. The problem of the colour of minerals belonging to the first category is complicated owing to the inclusion under this head of minerals which assume dilute colours due to the presence of some inclusions either solid, liquid or even gas, or due to some structural abnormalities in their crystal structure as that of blue halite. Further, under this head are also included all dilute colours produced by intermixture of foreign materials present in such a fine state of division that they cannot be detected even with the highest magnification.

It is gatherd from earlier works that a study of mineral colours offers considerable difficulties and it appears that no method proposed so far to investigate this problem has been found to be complete and convincing. W. Hermann[15] used a method which consisted of a study of the behaviour of a number of minerals and glasses artificially coloured with metallic substances and oxides, when subjected, at a given temperature, to the influence of different oxidising and reducing gases. He drew the following conclusions from the observed results: (i) The oxides of iron are the most important colouring agents. (ii) Manganese and chromium are next in importance. (iii) The rare earths uranium, cerium, thorium, etc., are practically of no importance as colouring agents. (iv) Certain organic substances may be present and act in conjunction with the metallic oxides as in the case of topaz. Brauns[16] after studying the influence of radium rays on the colour of some tinted minerals arrives at the conclusion that the colours must be due to some as yet unknown inorganic impurity in a diffused condition.

The literature about the coloured quartzes is rather enormous. Prominent amongst the coloured quartzes are smoky quartz, amethyst, rose quartz and blue quartz. The colour of smoky quartz is supposd to be due to atoms of free silicon. The cause of colour of amethyst and rose quartz is still unknown, but it is generally believed that they owe their colour to a metallic impurity, perhaps manganese, in a diffused condition. The colour of blue quartzes has been attributed to the presence of microscopically detectable inclusions in some cases and in others to the presence of metallic impurities in a fine state of division. It is held by many that the acicular inclusions observed in many of the blue quartzes are alone responsible for the blue colour.

The metallic impurities detected in the quartz specimens now under study are only two, *viz.*, titanium and iron. The Iron compound which occurs in these quartzes, as it is easily washed off by acids and as this washing by acids does not destroy the colour of the specimens, evidently does not contribute to the colour. The iron exists only as an external impurity, probably

as a hydrated oxide coating the individual grains of quartz and also filling in the cracks present both in the coloured and in the colourless specimens. The loss of weight suffered by the various specimens of quartz on heating them does not appear to signify anything as it is very slight and more or less the same in all the specimens, whether coloured or colourless. So now it is more or less definite that the colour of the charnockite and other quartz specimens studied here is due to the presence of titanium.

The acicular inclusions present in these quartzes were separated by hydrofluoric acid and on microscopic and chemical examination was found to be fine needles of rutile. To find out whether all the titanium detected in the individual quartz specimens was present in the form of rutile needles alone or also in some other state, the quantity of rutile present in the various specimens was estimated microscopically and was found to be roughly the same even in specimens of different intensities of colour. Since chemical analysis revealed that the intensities of colour was proportional to the titanium content of the specimens and as this titanium content was in great excess over that required by the amount of rutile present in it, it follows that the coloured specimens contained titanium not only in the form of rutile but also in some other form. Colourless quartzes which contained acicular inclusions showed only the amount of titanium corresponding to the amount of rutile present in them.

All the blue coloured quartzes invariably show the presence of a pale brownish-yellow turbidity in transmitted light the intensity of which varies with the intensity of the blue colour of the specimens in reflected light. It is also observed that this brownish-yellow turbidity is completely absent in all the colourless quartzes without any exception. Now it is interesting to note that the brownish-yellow colour observed in transmitted light is complementary to the blue colour observed in reflected light and both colours are destroyed by heat. It can be gathered now that the blue colour observed in these quartzes is due almost entirely to the existence of a brownish-yellow turbid medium which contains the excess titanium mentioned above, perhaps in a colloidal condition.

The brownish-yellow turbidity was not noticeable in the colourless quartz specimens from the Pallavaram (Madras) charnockites which contain the acicular and drop-like and dust-like inclusions in an exactly similar manner as the coloured specimens. Another colourless quartz obtained from Bodi (Madura) charnockite contained the drop-like and dust-like inclusions, but did not reveal the presence of either the acicular inclusions or of the brownish-yellow turbid medium. Further, a sample of fine opalescent blue quartz from a champion gneiss ($H_{11}/946$) of Kolar Gold Fields, Mysore, is

almost free from acicular inclusions, but shows the brownish-yellow turbidity to a marked degree and a titanium content (0·03% TiO_2) equal to that of the charnockite blue quartz. Two other samples of quartz, one from Chitaldrug granite (M_2/233), and the other from an unidentified gneissic rock from Holenarsipur (M_1/349), are completely free from acicular inclusions but contain the brownish-yellow turbid medium. They show a titanium content equal to those of the other coloured quartzes and their opalescent blue colour in reflected light is also sufficiently strong. So, from the observations given above, it can be gathered that the acicular inclusions are not responsible for the production of the brownish-yellow turbidity observed in the coloured specimens.

From general considerations of the theories of light scattering it is found that the opalescent blue colouring of such intensity as is met with in these quartzes would be prominent only when the particles producing it are of the order of thickness of 0·05 to 0·2 μ. The particles of such size cannot be seen clearly even in high power oil-immersion magnifications. No doubt particles finer than this are incapable of producing this type of opalescent colour which is partly a true opalescence and partly a colloidal colour. Thus, as the needles are of the average thickness of 0·8 μ, they will not be capable of producing the opalescent blue colour observed in these quartzes.

In the blue quartzes now under study the colour is only an opalescent colloidal one produced not by very fine particles of the order of molecular dimensions of titanium, but by considerably bigger colloidal particles of the magnitude of 0·2 to 0·05 μ in diameter. The colour produced is thus an almost intermediate one between a true colloidal colour and a true opalescent colour. Further, the colour produced would be modified to a very great extent by the absorption coefficient of the titanium compound composing these colloidal particles. Thus the presence of such big colloidal particles of the titanium compound in the quartz, no doubt, is responsible for both the brownish-yellow turbidity in transmitted light and the blue colour in reflected light.

The titanium compound composing these particles is perhaps capable of undergoing a physical or a chemical change on heating, interfereing thereby with its capacity to scatter light in a particular manner and thereby changing the nature of the scattered light. Thus the colour in this particular case would be lost on heating.

The dust-like and drop-like inclusions appear to be none other than some congealed glassy matter. It is definitely ascertained that they contain no titanium as these inclusions were found to occur with equal prominence in some of the colourless quartzes, like those from Bodi charnockite in which

titanium was completely absent. Perhaps a detailed study of these inclusions will reveal the exact origin of the charnockites.

Summary

Specimens of charnockite quartz with varying intensities of blue colour as well as specimens of opalescent blue quartz from the Champion gneiss and associated rocks of Mysore were examined both microscopically and chemically. The colour of these quartzes was found to be greatly affected by heating, the charnockite quartz losing its colour completely even at 300°.

All the coloured specimens and some of the colourless specimens show under the microscope two types of inclusions, (*i*) regularly arranged acicular inclusions, and (ii) drop-like and dust-like inclusions scattered throughout the quartz without much arrangement.

Invariably, all the coloured quartzes show a brownish-yellow turbidity in transmitted light, the intensity of which varies with the intensity of the blue colour in reflected light. This turbidity is destroyed by heat in the same way as the blue colour.

All the colourless quartzes, even those which contain all the other inclusions, are completely free from this turbidity.

The acicular inclusions were separated out from the quartz by dissolving the latter in hydrofluoric acid and they were then examined both microscopically and chemically. They are found to be very fine rutile needles.

Almost all the iron present in these quartzes is discovered to be only an external impurity and so appears to have nothing to do with the colour of these quartzes.

Titanium is the element which is responsible for the production of the turbid medium and the consequent colouration of the quratz. The intensity of colour is proportional to the titanium content of the specimen.

The amount of rutile is calculated from the micrometiric estimates of the number and size of the rutile needles and thus the amount of titanium required to form these needles is also derived. It was found that the quantity of rutile present was the same in specimens of quartz with different intensities of colour.

The titanium content of all the coloured specimens is in great excess over that due to the amount of rutile present in them.

There are found some coloured specimens of quartz which are completely free from any acicular inclusions, but at the same time exhibit the presence of the brownish-yellow turbid medium.

It was found that the acicular inclusions present in these quartzes was not responsible for the production of either the blue colour or the brownish-yellow turbidity, in these quartzes.

It is suggested that in these blue quartzes the colour is only an opalescent colloidal one produced by colloidal particles of the size of 0·2 to 0·05 μ in diameter. The colour produced is intermediate between true colloidal colour and true opalescent colour and it is modified to a great extent by the absorption coefficient of the titanium compound composing these colloidal particles.

The presence of these colloidal particles is responsible for the brownish-yellow turbidity as well as the blue colour. The loss of colour brought about by heating the quartz is due to a change in the physical or chemical properties of the titanium compound on heating.

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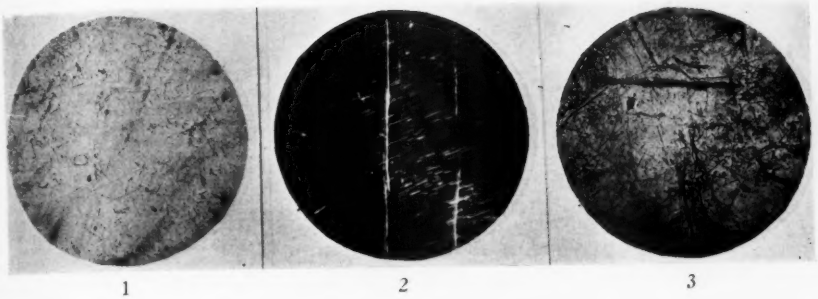

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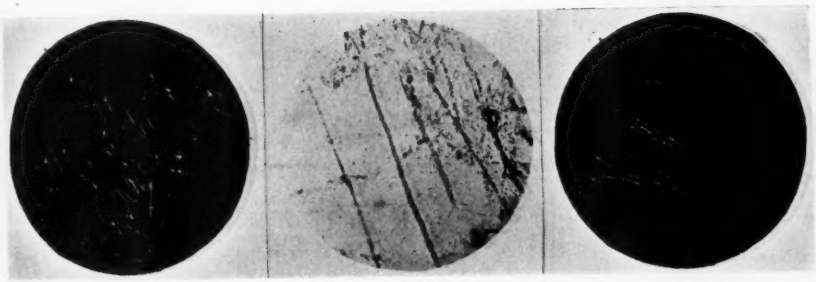

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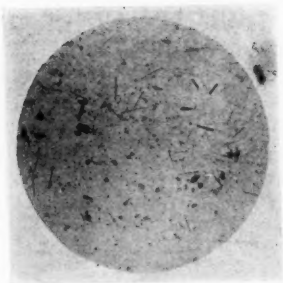

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EXPLANATION OF PLATE

1. A blue quartz section between parallel nicols. × 100.
   The acicular inclusions and the dust-like and drop-like inclusions.
2. A blue quartz section in dark-field illumination. × 150.
   The acicular inclusions.
3. Blue quartz " A " between parallel nicols. × 100.
   The dust-like and drop-like inclusions.
4. Blue quartz " C " in dark-field illumination. × 150.
   The dust-like and drop-like inclusions appearing as white cloudy patches.
5. Blue quartz " B " between parallel nicols. × 300.
   The dust-like and drop-like inclusions arranged in lines.
6. Blue quartz " B " in dark-field illumination. × 150.
   The dust-like and drop-like inclusions arranged in lines.
7. Rutile needles separated from the blue quartz.
   Slide in dark-field illumination. Negative print. × 100.

RAMAN EFFECT AND THE POTENTIAL FUNCTION OF THE ETHYLENE MOLECULE*

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1. Introduction and General Considerations

Soon after the fundamental discovery of Sir C. V. Raman, it was realized that a knowledge of the vibration spectra of molecules could also throw some light on the force system holding atoms together in the molecule. Of course, the vibrations considered being very nearly harmonic, the only immediate information to be expected is a knowledge of forces near the configuration of equilibrium of the molecule, in other words, the quadratic potential function of the deformed molecule.

In 1914 Bjerrum interpreted the vibration spectra of simple triatomic molecules as given by infra-red data, by means of either a central force field or a valency force field. Both hypotheses are mathematically equivalent, provided they are completely formulated; physically, however, they appear rather different. The valency forces hypothesis, completed by the adjunction of angular deformation forces, expresses very well the fundamental conceptions of stereo-chemistry as stated by Lebel, van't Hoff, Bæyer and others. On the other hand, one sees immediately that the number of force constants necessary to express the valency deformation potential field is usually much less than the symmetry of the molecule allows for.

It thus might seem quite irrelevant to the physical problem to introduce more force constants than just needed to express the valency deformation system. In fact, it is now known that such simple bindings as CH are very well explained, *i.e.*, up to a few per cent., by simple valency deformation forces. Moreover, there is no doubt that the valency forces hypothesis is essentially sound, since it is sufficient to qualitatively clear up the main aspects of the vibration spectra. The results given at length in the unique monographs of Kohlrausch affords the best proof. However, for more complicated bindings or heavy atoms, the simple valency forces hypothesis

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quite often does not lead to even an approximation of 10 or 20 per cent. In such cases, neither the valency forces nor the simple central forces hypothesis suffices ; it is necessary to include interaction between neighbouring bindings, in other words cross-terms in the potential function. The question then arises, what physically significant terms to choose among the manifold possibilities, considering that, in many cases, the problem is determinate from the mathematical point of view.

2. *Investigations on Molecular Potential Functions*

Let us consider the simple example of a triatomic symmetrical molecule XY_2. The vibration spectra is composed of two vibrations symmetric with respect to the axis, one valency or γ-vibration and one deformation or δ-vibration, and one anti-symmetric γ-vibration. Two force constants seem at first sufficient : f for the stretching of the bond and d for the angular deformation. On the other hand, the most general quadratic potential function compatible with the symmetry involved introduces three constants for the symmetrical deformations and one more for the anti-symmetrical deformation of the molecule. Moreover, the angle of the bindings still comes in as a parameter. Three data are obviously inadequate to give the answer. This explains why a calculation of the constants f, d and the angle, ignoring the interaction constants, has often led to deceptive results, in cases where a check on the angle could be obtained by interferometric methods. It is not because the interaction constants escape a direct determination, that they can be left out of consideration. On the contrary, one might rather hope to know more about chemical forces in the molecule by investigating with accuracy the magnitude of these interactions ; even the definite proof of their small value is of interest.

One means of getting the needed additional data for the problem has been provided for by the substitution of isotopic atoms in the molecule. This, however, proves useful only with deuterium. In the case of H_2O, for instance, the number of experimental data could rise to nine, exceeding largely the number of the constants to be determined, which puts the proposed potential function to a severe trial. *Cross and van Vleck* have investigated that problem, with a lesser number of data. A difficulty one immediately meets with in such problems is the influence of anharmonicity, that can even match the effect of the small interaction terms. Most of the authors have usually corrected rather arbitrarily the data, which leaves some doubt about the real physical significance of the smaller force constants they obtain. We believe that the difficulty can be coped with in a better way, as shall be seen later.

One might prefer to approach the problem from a less general point of view, trying to improve the valency force field by superposing on it a small central field correction. This has been done with success for tetrahedral molecules by *Urey and Bradley* and much extended by *Nagendra Nath.* A later investigation of the vibration frequencies of the several dueteromethanes by *Rosenthal and Voge* proved, however, the necessity of resorting to the most general potential function.

One of us, considering the benzene molecule with its many deuterosubstitutes as a promising field, investigated the theoretical problem in its complete generality for a molecule of the type $X_6 Y_6$. It seems that unexpected difficulties from the chemical side have delayed the publication of the vibration spectra of the complete set of deuterobenzenes.

3. *The Deuteroethylenes—Earlier Investigations*

Another interesting and fundamental molecule is the ethylene. It has been studied experimentally by several workers, both in the Raman effect and in the infra-red, more recently by *Bonner* and *Glockler.*

The first theoretical investigation of the C_2H_4 molecule is due to *Sutherland and Dennison.* These authors considered simply the group of five plane frequencies (three Raman and two infra-red) symmetrical with respect to the CC-axis. They took a potential function with four constants, with no coupling between the two CH_2 groups nor between each group and the double bond CC. Their aim was to test the hypothesis, suggested by chemistry, of the independence of the groups CH_2 in the molecule. A potential function with but four constants for five frequencies of vibration involves a relationship between these frequencies, approximate fulfilment of which is a check upon the hypothesis.

At the same time, *Delfosse* had made an independent study of the same molecule, extended to the nine plane vibrations, assuming a thirteen constants potential function. The physical meaning of it was that he considered all the possible interactions in the interior of each group CH_2 and between the two groups. The result again proved the small importance of the constants of interaction.

The assignments and values of some fundamental frequencies (especially group S_2, see below) were still very uncertain. The experimental work of Bonner improved much the situation. He also gave an approximate potential function involving six constants, which, however, could not reproduce in a satisfactory way his new accurate data.

4. *The Deuteroethylenes—Recent Work*

We thought it worthwhile to start in this Institute a systematic experimental and theoretical investigation of the Raman spectra of the ethylene molecule together with its six deuterosubstitutes C_2H_3D, $C_2H_2D_2$ (*Cis trans* asymmetrical), C_2HD_3, C_2D_4. The technique used and the results have been published by *de Hemptinne* and his collaborators. All Raman spectra have been obtained under the same conditions, at the boiling temperature. The infra-red spectrum was not observed, but Bonner's determinations for C_2H_4 and later Sutherland's for C_2D_4 were used for the theoretical work.

At the same time, one of us (C.M.) with *Verleysen* computed first from Bonner's results a more accurate potential function for the vibrations in the plane of the molecule involving eleven constants and reproducing his data with less than 0·15 per cent. error. This potential function (we call it M.V.) was the starting point for computing the vibration spectra of C_2D_4 and the three $C_2D_2H_2$. The first deuteroethylene obtained in the laboratory in a sufficiently pure state was C_2H_3D. Using M.V.'s potential function, the theoretical spectrum was computed by *Lemaître and Tchang*, showing a very good agreement with the experiment: seven out of nine possible Raman frequencies observed, with no greater discrepancy than 1·4 per cent. Later experimental determinations of Raman frequencies of the $C_2H_2D_2$ and C_2D_4 molecules showed agreement only within 3·5 per cent., with one exception for C_2D_4 where a single discrepancy of 5·5 per cent. occurred. Experimental information about the completely symmetric C_2D_4 enabled to correct immediately the M.V. potential function. *Tchang* obtained a new one (we call it Tchang's function) with fifteen constants, paying due regard to the anharmonic correction, as will be seen. The final agreement is shown in Table II below.

5. *Calculation of the Normal Modes for the Isotopic Molecules*

In the following, we are concerned only with the nine plane fundamental modes of vibration. As is well known, in the case of the completely symmetrical molecules C_2H_4 and C_2D_4, the modes divide into four independent families.

If S and A mean, respectively, motions of the molecule symmetric and anti-symmetric with respect to the centre of the molecule; π and σ, plane motions symmetric and anti-symmetric with respect to the CC-axis; π' and σ' the same with respect to the perpendicular axis in the plane of the molecule, we have

$$3\,S_1\,(\pi\pi') \qquad 2\,A_1\,(\pi\sigma') \qquad 2\,A_2\,(\pi'\sigma) \qquad 2\,S_2\,(\sigma\sigma'),$$

where the numerals indicate the number of modes in each family. Their

approximate form is given for C_2H_4 in Fig. 1. Excepting the deformation or δ-frequency of each of the families S_2 and A_2, the assignment of the experimental frequencies is quite sure. Owing to the symmetry of the molecule with respect to a centre, the modes S are all Raman active and inactive in absorption ; the converse is true for the modes A.

We have admitted in all the computations the frequency assignment of Bonner (see Table II). The configuration of the molecule is also taken as with Bonner : angle HCH = 126°, distances CC = 1·37 and CH = 1·04 Angström units. The more recent values given by *Penney* are probably somewhat better, but cannot change much our results.

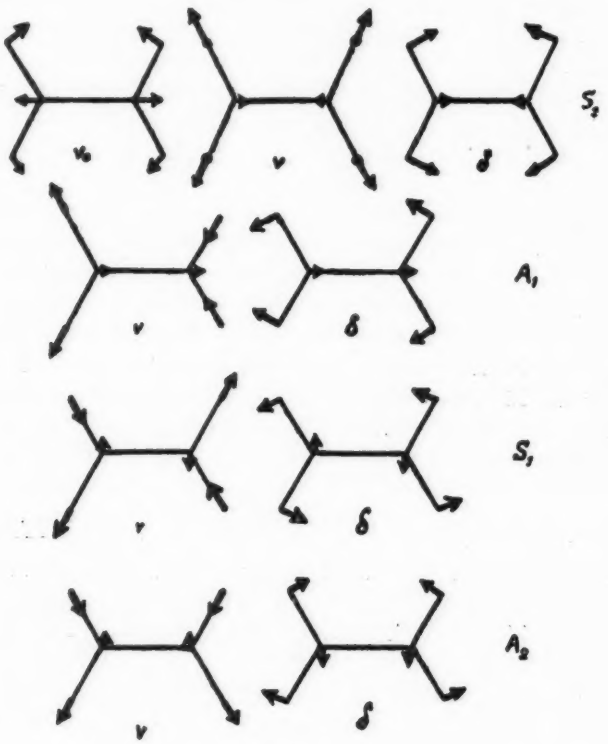

FIG. 1

We have made use of " symmetrical co-ordinates " ; they have the property of being zero for any mode which does not belong to the symmetry family corresponding to the co-ordinate considered.

For each family, as many co-ordinates are needed as there are modes in that family. The symmetrical co-ordinates are simple linear functions of the cartesian co-ordinates of the masses. From their definition follows immediately their most useful property: the most general quadratic potential energy expressed in terms of symmetrical co-ordinates splits in as many partial functions as there are families of different symmetries. In other words, there cannot be quadratic "cross-terms" involving two co-ordinates of different symmetries. This property, however, does not hold for terms higher than the second degree; but we do not consider here these anharmonic terms.

The separation obtained for the potential function also holds for the kinetic function, so long as the masses show the symmetry of the forces in the molecule. The problem then reduces to four partial problems; for each, determinantal equation gives the frequencies and the normal modes as linear functions of the symmetrical co-ordinates.

If, on the other hand, we consider the isotopic molecules of ethylene, the symmetry of the potential function is preserved, but that of the masses diminishes or disappears and the kinetic energy, expressed in symmetrical co-ordinates is no longer separable in four independent parts, but contains "cross terms" involving co-ordinates with different symmetries. So, for each of the three molecules $C_2H_2D_2$, there are two families of modes of lesser symmetry than before, which appear each as the result of coupling together two of the four modes of the C_2H_4 molecule. We have, with obvious notations

trans	5 S $(S_1 S_2)$	4 A (A_1A_2)
asym.	5 π (S_1A_1)	4 σ (S_2A_2)
cis	5 π' (S_1A_2)	4 σ' (S_2A_1)

For the two C_2H_3D and C_2HD_3 molecules, no separation at all subsists and the algebraic problem is of the ninth degree. The expansion of such a determinantal equation is prohibitive. But for computational work there is no reason why the equation should be written explicitly as a polynominal expanded in powers of the unknown frequency. Instead, starting from the nine Lagrange equations, *Lemaître* has given a very easy method for solving numerically the problem. In these calculations, it is convenient to add the two translations and the rotation as modes of vanishing frequency; each symmetry family then contains three modes.

6. *Numerical Value of the Potential Function*

Influence of the Interaction terms.—From the preceding section follows that the most general potential function for the modes S_1 contains 6 constants,

whereas each of the others only 3 ; thus altogether 15. We call them the *symmetrical potential constants.*

The simple valency deformation hypothesis, on the other hand, calls only for four constants : two for the stretching of the CC- and CH-bonds, one for the deformation of the angle HCH and another related to the deformation of the angle HCC. It has been shown elsewhere that eleven more interaction terms can, in a non-ambiguous way, be added to the principal terms : one involving the interactions of neighbouring CH-stretchings, two for non-neighbouring ones ; two for the interactions between the angles ; four for the interactions between angles and CH-stretchings (we call these g-interaction terms) ; finally one for the interaction of the CC- and CH-stretchings (we call it f_c) and one for the interaction of the CC-stretching and the angle HCH (we call it γ_c). These last two terms occur only for the modes of symmetry S_1 because for the other symmetries the distance CC does not vary. All the other interaction constants and also the principal constants appear in several or all modes of symmetry. We call all these the *valency potential constants.* They are linearly related with the symmetrical constants.

When we started the work, only the frequency values for plane vibrations of C_2H_4 given by Bonner were at our disposal ; hence 9 data for determining the 15 constants of the potential function. As already said, Bonner did not reach a satisfactory accuracy using a function with 6 constants, the four principal ones *plus* a term coupling neighbouring CH-stretchings and another one coupling the angles. Considering separately the S_1 family, for which the data are accurate to about 1 cm.$^{-1}$, one has to determine 6 " symmetrical " constants with only 3 data ; for all other families, there are 2 data for 3 constants. In all cases one of the symmetrical constants only depends on the g-interaction terms. *Cross and van Vleck* found that the g-term is the smallest of all hoping only about a fifth of the value of the interaction term between stretchings, in the case of the H_2O molecule. We accordingly put the four g's equal to zero and were left with a potential function with 5 constants for the family S_1 ; the three remaining functions could be determined immediately. Due to the non-linear character of the relations connecting the frequencies with the constants of the potential function (these are the classical symmetric functions of the roots of a cubic), it was necessary to introduce both interaction terms f_c and γ_c between the CC-bond and the group CH_2, otherwise no real solution could be obtained. The necessity of the two terms expressing that interaction had hitherto not been recognised ; later *Linnett and Thompson* came to the same conclusion. From our computed potential function, it thus appeared that the *most important interaction terms in the* C_2H_4 *molecule are neither the internal interaction terms of the groups* CH_2,

nor the external interaction of one group CH_2 *upon the other, but rather the interaction of the double bond CC with the attached groups* CH_2. This conclusion is entirely substantiated by the subsequent still more accurate work of *Tchang* already referred to.

For the high S_1 frequency 3019 cm.$^{-1}$ (in the gas) only the f_c coupling term has some importance ; it increases the potential energy by about 5 per cent. For the medium S_1 frequency 1621·3 cm.$^{-1}$ and the low S_1 frequency, 1344 cm.$^{-1}$, only the term γ_c has importance ; it decreases the potential energy in the first case and increases it in the second by about 20 per cent. The computation of the normal modes shows that in the high frequency vibration, 93 per cent. of the total potential energy is concentrated in the stretching of the bonds CH ; the relative amounts of potential energy localised in the deformation of the CH-bond, of the HCH-angle and of the CC-bond respectively are 1 : 3, 7 : 10 for the 1621 cm.$^{-1}$ vibration and 0 : 1 : 10 for the 1344 cm.$^{-1}$ vibration. It thus appears that the usual view ascribing the medium frequency 1621 cm.$^{-1}$ to a stretching of the double bond and the low frequency 1344 cm.$^{-1}$ to a deformation of the angle HCH is only a very conventional one. The inspection of the displacements of the atoms in the corresponding modes also confirms this remark ; in the medium frequency mode, the H atoms and the C atom of a group CH_2 swing in nearly opposite directions whereas in the low frequency mode, they swing in nearly the same direction. One could conclude the argument saying that in the C_2H_4 molecule there is a rather strong coupling between the deformation vibration of a free group CH_2 (about 1444 cm.$^{-1}$, taken from the A_1 family and from direct computation) on the one hand, and the valency vibration of the group C : C or H_2C : CH_2, considering now CH_2 as a rigid system (*i.e.*, by computation, 1570 for C : C and 1455 cm.$^{-1}$ for H_2C : CH_2). Analogous remarks can be developed for the C_2D_4 molecule ; in this case, however, the coupling considerated is much less than for C_2H_4.

7. Computation of the Frequencies and Normal Modes of the Deuteroethylenes

The two important interaction terms between the double bond and the group CH_2 are not fully determined by data from C_2H_4 only although their values are rather narrowly restricted. Choosing a reasonable but still somewhat arbitrary value for one of them, a first prediction of the frequencies to be expected for the deuteroethylenes was obtained on the basis of the M. V. potential function. This helped very much to identify the observed frequencies, as the discrepancies between computed and observed frequencies never exceeded 5 per cent. and in most cases did not exceed 1·5 per cent. The larger discrepancy was always observed for the " medium " frequency, near 1500 – 1600 cm.$^{-1}$, and increased regularly from C_2H_4 to C_2D_4. This

frequency precisely is very sensitive to the relative values of the two mentioned interaction terms. A comparison with the experimental value 1567 cm.$^{-1}$ for *cis* and *trans* $C_2H_2D_2$ enabled to find the correct values of the two hitherto approximately known interaction constants.

With the help of the M. V. potential function, the normal modes were also calculated for all isotopic molecules, excepting C_2HD_3. The modes of C_2H_3D are reproduced in Fig. 2. The amplitudes are given in 10^{-9} cm. units ; they have been calculated on classical grounds by assuming an energy

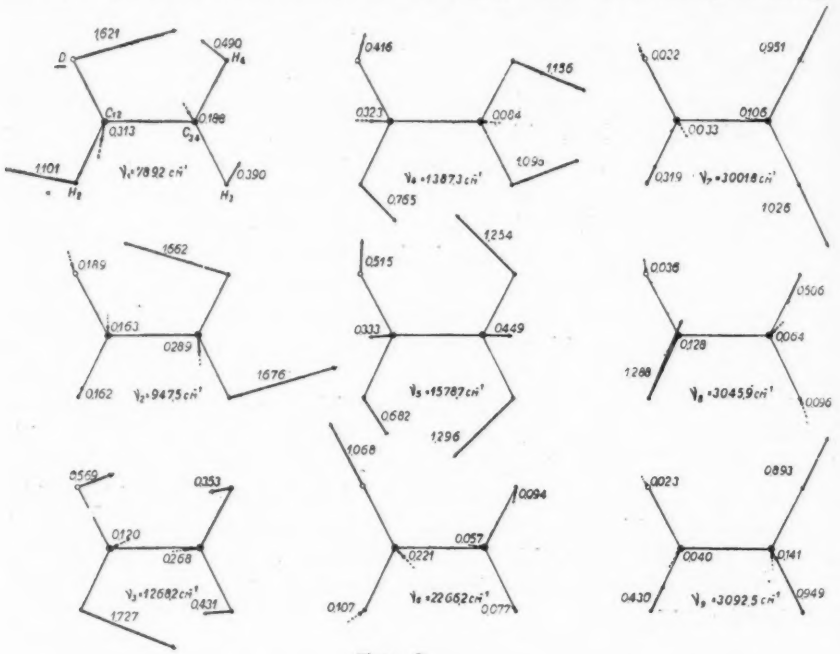

FIG. 2

"Normal modes of vibration of the C_2H_3D molecule." Units 10^{-9} cm.

of the vibration equals h times the frequency. One fact strikes immediately : although the symmetry of the masses has disappeared, still the modes show roughly some symmetry properties, *e.g.*, symmetry with respect to the carbon-axis for the modes at 1387 cm.$^{-1}$, 1579 cm.$^{-1}$, 3002 cm.$^{-1}$ and to a lesser extent 1268 cm.$^{-1}$; antisymmetry with respect to the same axis for the modes at 789 cm.$^{-1}$, 947·5 cm.$^{-1}$ and 3092·5 cm.$^{-1}$ The modes at 3046 cm.$^{-1}$ and 2266 cm.$^{-1}$ have a composite character ; in fact their energy can be apportioned in the following way between the motions having the symmetries of the C_2H_4 molecule : for 3046 cm.$^{-1}$, S_1 34·9 per cent., A_1 8·1 per cent., A_2 7·1 per cent.,

S_2 49·9 per cent. ; for 2266 cm.$^{-1}$, S_1 27·2 per cent., A_1 29·8 per cent., A_2 20·7 per cent., S_2 22·3 per cent. whereas for 1579 cm.$^{-1}$, S_1 91·5 per cent., A_1 7·8 per cent., A_2 0·4 per cent., S_2 0·3 per cent.

One notices also the nearly independent motions of the two groups CHD and CH_2 in the molecule. From these results, qualitative prediction of the intensities (and even polarisations) can be made which check very well with the observed Raman intensities. The relative intensities of the infra-red bands and their form can easily be deduced also, but the absorption of the molecule $C_2 H_3 D$ has not yet been studied.

Finally, there is a very close connection, for all deuteromolecules, between the modes of vibration and the frequency spectrum : the nearer a frequency of $C_2 H_3 D$, $C_2 H_2 D_2$ lies to a frequency of the completely symmetric molecule $C_2 H_4$ or $C_2 D_4$, the more the corresponding mode of vibration resembles the neighbouring mode of $C_2 H_4$ or $C_2 D_4$. In the application of this rule to the molecules $C_2 H_2 D_2$, only those neighbouring modes of $C_2 H_4$ and $C_2 D_4$ are to be considered, which possess the symmetry of the mode investigated. This remark explains the highly symmetrical character of the mode 1579 cm.$^{-1}$ of $C_2 H_3 D$, lying quite near to the 1623 cm.$^{-1}$ of $C_2 H_4$ and the corresponding one of $C_2 D_4$. The same holds true for the " medium " frequency of the other molecules. On the other hand, the composite mode 2266 cm.$^{-1}$ of $C_2 H_3 D$ partakes of the four different symmetries of the four neighbouring modes of $C_2 D_4$ (see Table II). One could easily propose for the modes notations expressing the main features of the motions of each CHD and CH_2 group ; such one has been used above for $C_2 H_2 D_2$, another has been proposed by *Ta You Wu* for $C_2 H_3 D$.

It has been also possible, due to the feeble interaction between the two groups containing the hydrogen or deuterium atoms, to select or to compute the three " fundamental frequencies " of each of the isolated groups CH_2, CHD, CD_2. These data help characterising the modes of vibration of the deuteroethylenes.

In the case of the three $C_2 H_2 D_2$ molecules, there are always two γ-CH frequencies near 3000 cm.$^{-1}$ and two γ-CD frequencies near 2200 cm.$^{-1}$. In all these cases, each frequency of $C_2 H_2 D_2$ lies nearly exactly at the middle position between the two $C_2 H_4$ or the two $C_2 D_4$ frequencies, which by their coupling, as explained above, produce the frequency of $C_2 H_2 D_2$ considered. At the same time, the produced mode of vibration proves to be very nearly the vectorial sum of the displacements of the atoms existing in each of the two composing modes. As a consequence, in the 3000 cm.$^{-1}$ group of frequencies the displacements of the two heavy D-atoms nearly cancel, whereas in the

2200 cm.$^{-1}$ group of frequencies the displacements of the two light H-atoms nearly cancel.

8. Tchang's Potential Function—Anharmonicity of the Vibrations

As soon as the Raman and the infra-red spectra of $C_2 D_4$ were known, enough data were available to determine all the three constants of the potential functions of the families A_1, A_2 and S_2. The four experimental frequencies for each family (two for $C_2 H_4$, two for $C_2 D_4$; one A_2 not observed for $C_2 D_4$) have to verify a theoretical relation involving the masses only ; for A_1 and A_2 it is

$$\frac{\nu'_H \, \nu''_H}{\nu'_D \, \nu''_D} = \sqrt{\frac{\mu_D \, m_D}{\mu_H \, m_H}} = R_{th} \qquad \mu_H{}^{-1} = m_C{}^{-1} + m_H{}^{-1}.$$

The relation for S_2 is a little more complicated, containing the distances and angles of the atoms in the molecule. These theoretical " isotopic ratios " R_{th} are only approximately verified by the data ; the departure, shown in the table, amounts to a few per cent. less for the experimental ratio R_{exp}. This is evidently due to the anharmonicity of the vibrations in the $C_2 D_4$ molecule being less pronounced than in $C_2 H_4$, which corresponds to the theoretical expectation. The difference between R_{th} and R_{exp} measures the sum of the differential anharmonicities of the vibrations within a same family in the two molecules. At first, it seems illusory to try to obtain the interaction terms in the potential function with an accuracy greater than or comparable to the influence of the anharmonicity upon the results.

The same remark holds for the S_1 family, where six very precise experimental data are now at hand, which have to fulfil the relation

$$\frac{(\nu' \, \nu'' \, \nu''')_D}{(\nu' \, \nu'' \, \nu''')_H} = \frac{m_D}{m_H} = R_{th}.$$

The five independent data are not sufficient to determine the six " symmetrical " constants of the potential function of the S_1 family. As already said use is made of the very accurate 1567 cm.$^{-1}$ *cis* and *trans* frequency to complete the determination.

TABLE I

	S_1	A_1	A_2	S_2
R_{th} ..	1,998	1,868	1,868	1,666
R_{exp} ..	1,954	1,827	..	1,624
R_{spec} ..	1,954	1,824	1,824	1,629

Lemaître suggested to choose new empirical values for the masses m_H and m_D; we call them " spectroscopical masses " m'_H and m'_D, without attaching any special physical meaning to the word. They must be such that, when substituted in the " isotopical relations ", they give for S_1 the actual value $R_{exp} = 1{,}954$ instead of the theoratical one $R_{th} = 1{,}998$. This only determines their ratio. We then obtained the separate values of m'_H and m'_D by the relations

$$m'_H = m_H \left(1 + \frac{c}{\sqrt{m_H}}\right)$$

and a similar one, with same value of c, for m'_D. This is, to the approximation considered, nothing but a direct transcription of the well-known formula for the frequency of an anharmonic oscillator, as has already been shown in another work. (Manneback, benzene molecule). *Tchang* found for S_1 the values

$C = 0{,}080$ $\quad m'_H = 1{,}088$ $\quad m'_D = 2{,}126$

$\quad\quad\quad

TABLE II

		Calculated			Observed de Hemptinne, Suth., Bonner		Calc. Tchang — observed in per cent.
		M.V.	Thomp., L.	Tchang			
C_2H_4	S_1 ..	3019.0	3018		3007		
		1621.3	1623	..	1621		
		1343.9	1343		1341		
	A_1 ..	2988.0	2993		2988		
		1444.0	1444		1444		0.0
	A_2 ..	3107.0	3101		3107		
		949.7	950		949.7		
	S_2 ..	3069.0	3114		3072		
		950.0	1203		950	(943)	
C_2H_3D	..	3092.5		3094	3104	(0.5)	− 0.3
		3045		3039	3016	(9)	0.8
		3002		2986	2965	(2)	0.7
		2266		2272	2266	(1.5)	0.3
		1579		*1600*	*1600*	(10)	− 0.0
		1387		1393	1397	(5)	− 0.3
		1268		1269	1285	(6)	− 1.2
		947.5		948	..		
		789		799	..		
$C_2H_2D_2$ *Cis*	π' ..	3065		3056	3046		0.3
		2304		2295	2290		0.2
		1516.5		*1570*	*1567*		0.2
		1248		1222	..		..
		753		759	763		− 0.5
	σ' ..	3031		3033			
		2229		2249	1282		0.9
		1295.4		1293			
		820		831			
trans	S	3049		3038	3033		0·2
		2291		2277	2276		0·05
		1514		*1567*	*1567*		0·00
		1240		1213	1214		0·1
		808		818			
	A ..	3053		3053			
		2233		2260			
		1308		1310			
		765		774			
asym	π ..	3004		3005			
		2221		2232	2221		0·5
		1555		*1588*	*1581*		0·4
		1358		1361	1379		− 1·3
		1043		1033			
	σ ..	3088		3090			
		2316		2322			
		945·6		946			
		725		741			

TABLE II—(*Contd.*)

		Calculated			Observed de Hemptinne, Suth., Bonner	Calc. Tchang — observed in per cent.
		M.V.	Thomp., L.	Tchang		
C_2HD_3	..			3045		
				2352		
				2274	2272	0·1
				2227	2215	0·5
				1548	*1545*	0·2
				1256		
				1028		
				811		
				720		
C_2D_4	S_1 ..	2284	2160		2251	
		1429	*1686*		*1515*	
		1009	902		981	
	A_1 ..	2152·5	2101		2192·3 (2199)	
		1073	1187		1077·4 (1081)	0·0
	A_2 ..	2325	2291		2340 (2353)	
		678	742		..	
	S_2 ..	2308	2323		2304	
		758·3	1016		780	

9. *Discussion of Results*

The two first columns give the frequencies calculated from the M.V. potential function (11 constants) and the Thompson-Linnett potential function (5 constants). Both potential functions have been computed from the same data given by Bonner, for C_2H_4 only, *i.e.*, (in cm.$^{-1}$)

S_1 (3019, 1623, 1342) ; A_1 (2988, 1444) ; A_2 (3107, 950) ; S_2 (3069, 950).

The frequencies chosen were all observed in the vapour state, with the exception of the S_2 frequencies observed in the liquid. The only interaction constant admitted by Thompson-Linnett[1] is our γ_c. They also computed the S_1 frequencies with a potential function not containing that interaction term and obtained the values

C_2H_4 : 3014, *1723*, 1230 cm.$^{-1}$; C_2D_4 : 2166, 1780, 866.

Tchang's potential function is based on the data from C_2H_4 and C_2D_4 and the 1567 *trans*-frequency ; it contains 15 constants, which is the maximum possible, *plus* the spectroscopic masses, which amounts to one more constant

[1] The " medium " frequency calculated by these authors for C_2D_4 is *larger* than the one calculated for C_2H_4. This evidently violates the rule proved by Lord Rayleigh (Theory Sound, I ; art. 88) that an increase of mass in a system cannot be accompanied by an increase of the fundamental frequencies.

for the anharmonicities. The recomputation of the C_2H_4 and C_2D_4 frequencies reproduced the experimental data used for calculating the potential function to within 0·1 per cent.; they are not reproduced in the table. For obtaining Tchang's function, only the Raman frequencies observed by de Hemptinne and his collaborators in the liquid state have been used.

The infra-red data, used (A_1 and A_2), however, were all obtained in the vapour, by Bonner for C_2H_4, by Sutherland for C_2D_4. This, of course, introduces some slight inconsistency in the whole scheme, but we thought this would be still better than to correct rather arbitrarily the experimental values for reducing them all to the same physical state. There is one case, the $C_2H_2D_2$ *trans*, in which the inconsistency has no effect, because all Raman lines S are obtained by the fusion of the modes S_1 and S_2 of the completely symmetrical molecules, whose frequencies are all taken in the same physical state. It is just that molecule for which the discrepancies between calculated and observed frequencies are systematically less than for any other.

All "observed" lines are Raman lines, except those listed under A_1 and A_2. The observed A_2 2340 cm.$^{-1}$ frequency in C_2D_4 is now given by Sutherland as 2353 ± 10 cm.$^{-1}$. Moreover, Sutherland[2] casts serious doubts upon the ordinary identification given above for both low frequencies of A_2 and S_2 in C_2H_4 and S_2 in C_2D_4. He proposes to consider these as the frequencies of the non-plane modes of vibration, the active infra-red one and of the active Raman one; the third, totally inactive, being probably near 800 cm.$^{-1}$. If we adopt this identification, two plane modes are still to be found.

Accepting the view, the observed Raman line 763 cm.$^{-1}$ attributed by us to $C_2H_2D_2$ *cis* would rather be the frequency of a Raman active non-plane mode of $C_2H_2D_2$ *asym*. Moreover, one faint unclassified Raman line at 863 cm.$^{-1}$ would be the non-plane frequency of $C_2H_2D_2$ *trans*. One of us with *Bernard* verified that these assignments are in good agreement (1·5 per cent.) with the values computed from Sutherland's assignment for C_2H_4 and C_2D_4.

One may ask whether these modifications in the fundamental frequencies will not alter appreciably Tchang's potential function. It certainly will modify two terms depending directly from the changed frequencies, but we believe that the reaction upon the rest of the calculated spectrum will remain exceedingly small, because in the present potential functions the high and the low frequencies of the family A_2 correspond to modes that are nearly not coupled at all; the same is true for the two modes S_2.

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[2] We thank Prof. Sutherland for kindly sending us his manuscript before publication.

In the following table, we give Tchang's values for what we called the "symmetrical potential" constants. The last decimal place given has, of course, no physical significance any more. F means the constant of the

TABLE III

S_1	A_1	A_2	S_2
$F = 9{,}356$			
$\phi_1 = 5{,}446$	$\phi_2 = 5{,}372$	$\phi_3 = 5{,}399$	$\phi_4 = 5{,}421$
$\gamma_1 = 1{,}276$	$\gamma_2 = 1{,}121$	$\Gamma_3 = 0{,}615$	$\Gamma_4 = 0{,}373$
$g_1 = 0{,}184$	$g_2 = -0{,}190$	$g_3 = +0{,}550$	$g_4 = -0{,}378$
$F_c = -0{,}387$			
$\gamma_c = -0{,}691$		units 10^5 dyn-cm.	

CC-stretching, the ϕ's are the constants of the CH-stretching, the γ's times l^2 those of the angle α = HCH, the Γ's times l^2 those of the angle β made by the bisector of the group CH_2 with the direction CC; the interaction constants are respectively defined by the following terms in the potential energy ($l_i = \overline{eH_i}$)

$$S_1 \begin{cases} u_1 = \Delta l_1 + \Delta l_2 + \Delta l_3 + \Delta l_4 \\ v_1 = l(\Delta\alpha_{12} + \Delta_{34}) \\ w_1 = \Delta L \end{cases}$$

$$A_1 \begin{cases} u_2 = \Delta l_1 + \Delta l_2 - \Delta l_3 - \Delta l_4 \\ v_2 = l(\Delta\alpha_{12} - \Delta\alpha_{34}) \end{cases}$$

$$A_2 \begin{cases} u_3 = \Delta l_1 - \Delta l_2 - \Delta l_3 + \Delta l_4 \\ v_3 = l(\Delta\beta_{12} - \Delta\beta_{34}) \end{cases}$$

$$S_2 \begin{cases} u_4 = \Delta l_1 - \Delta l_2 + \Delta l_3 - \Delta l_4 \\ v_4 = l(\Delta\beta_{12} + \Delta\beta_{34}) \end{cases}$$

$$2U = \sum_i^4 2U_i$$

$$2U_1 = \frac{1}{4}\phi_1 u_1^2 + \frac{1}{4}\gamma_1 v_1^2 + Fw^2 + g_1 u_1 v_1 + f_c u_1 w + \gamma_c v_1 w$$

$$2U_2 = \frac{1}{4}\phi_2 u_2^2 + \frac{1}{4}\gamma_2 v_2^2 + g_2 u_2 v_2$$

$$2U_i = \frac{1}{4}\phi_i u_i^2 + \Gamma_i v_i^2 + g_i u_i v_i \qquad (i = 3, 4)$$

The symbols Δ mean algebraic increases; the two angles β are counted positively clockwise. The differences in the ϕ's, γ's, Γ's amount to couplings between the stretchings CH and between the angles α and β. The indices correspond to the molecule $\overset{H_1}{H_2}C : C\overset{H_4}{H_3}$.

If there existed no interaction between the two groups CH_2, all quantities with index 1 and 2 would be equal, and the same for 3 and 4. Hence the corresponding differences $\phi_1 - \phi_2$, etc., measure the interactions of one group CH_2 upon the other $\phi_1 + \phi_2 + \phi_3 + \phi_4$, which is nearly zero, measures the interaction between the two bonds CH in the same group.

As a conclusion, we should like to stress the fact that 32 *Raman lines* plus 7 *infra-red bands have been accounted for with an accuracy never less than* 1·3 *per cent. using a potential function with* 15 *constants* plus *one anharmonic constant.* The average discrepancy between calculated and observed frequencies is 0·24 per cent. We believe, this is in favour of the physical reality of the interaction terms introduced in the potential function.

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